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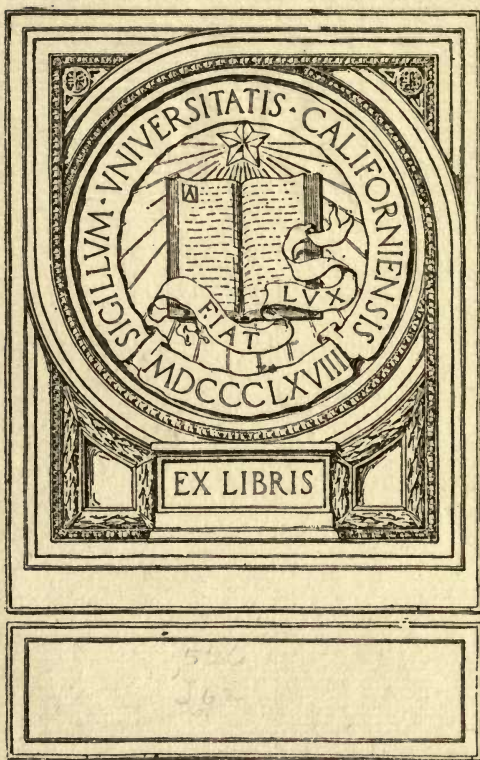
E. JOBLING

CATALYSIS
AND ITS
INDUSTRIAL APPLICATIONS

Text-books of Chemical Research and Engineering.

Edited by W. P. DREAPER, F.I.C.

CATALYSIS

AND ITS

INDUSTRIAL APPLICATIONS

BY

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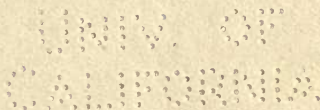
PREFACE

THE subject-matter of this book appeared originally in THE CHEMICAL WORLD. The outbreak of war and the fact that the author accepted a commission in His Majesty's forces has made it impossible to add certain additional details as originally intended. The subject-matter, therefore, remains in practically its original form.

THE EDITOR.

CONTENTS

Catalysis and its Industrial Applications.

CHAPTER I.

INTRODUCTION.

IT is a matter of common observation that many chemical reactions which normally proceed slowly, often so slowly as to be overlooked, can be accelerated to a greater or less degree by the introduction of some foreign material. The importance of this phenomenon—defined as far back as 1835 by Berzelius, as *catalytic*—will be at once evident, for by means of it, the technologist is able to effect readily reactions which would otherwise be either impracticable or impossible. More than a dozen years ago, Ostwald predicted that the great advances of chemical industry would be made through the more extensive employment of catalytic means, and his words have already found ample fulfilment in the establishment of new industries, as well as the further development of the old. The attention which the subject is receiving nowadays at the hands of industrial chemists justifies a hope of still more valuable application in the future.

GENERAL CONSIDERATIONS.

Before defining the term *catalyst*, the general question of reaction velocity demands attention. Reactions may be roughly divided into two classes : (1) those termed " ionic," which are practically instantaneous reactions ; and (2) those which, like the saponification of fats, take an appreciable time to attain equilibrium. Obviously, catalytic phenomena are concerned only with the latter, and particularly with that section of them which proceed so very slowly that no reaction appears to be taking place at all.

Now, the velocity of a reaction may be expressed in the following terms :—

$$\text{reaction velocity} = \frac{\text{chemical force}}{\text{chemical resistance}}$$

from which it follows that any alteration in chemical force or chemical resistance will correspondingly affect the reaction velocity. Thus, since rise of temperature both increases the chemical force and decreases the chemical resistance, the reaction velocity will be appreciably increased, which is in accordance with the general observation that a rise of $10°$ C. in the temperature usually more than doubles the velocity of the reaction.   Increasing the viscosity, on the other hand, by increasing the chemical resistance decreases the reaction velocity, as exemplified by Raschig's recent method for the manufacture of hydrazine, where the velocity of one of two simultaneous reactions is so reduced that a large percentage yield of the product of the other reaction can be obtained.

Again, the law of Mass action, according to which the reaction velocity is proportional to the concentrations of the reacting bodies, suggests another means for adjusting the reaction velocity,

viz., by variation of the respective concentrations. Still other factors, such as light, pressure, etc., are available for the same purpose.

The employment of any of these factors, however, is not generally advantageous. Increase of temperature is often injurious in technical processes, whilst the influence of the remaining factors is usually so small as to be almost negligible. Other means of diminishing the chemical resistance, preferably without increasing the chemical force by the expenditure of energy, are therefore desirable, and it is here that the full utility of catalysis appears. In the following pages many examples will be brought forward of an impractically slow reaction which has been found to be capable of acceleration to the point of commercial success, without the expenditure of energy and at ordinary temperatures, merely by the assistance of a catalytic means.

Of the many definitions of the term *catalyst* and their respective merits, it is impossible to speak here. Ostwald's definition, which, by reason of its authoritativeness, has obtained general acceptance, states that " a catalytic agent is that material which affects the velocity of a chemical reaction without appearing in the final products." The definition, though open to objection on several grounds, may at least be accepted as setting forth the two main criteria of a catalytic process. These and other characteristics will now be discussed, together with considerations that arise therefrom.

CHARACTERISTICS OF CATALYTIC REACTIONS.

(1) NEGATIVE CATALYSIS.

From the definition given above, it is evident that the effect of a catalyst may be either positive or negative, *i.e.*, the catalyst may either accelerate

or retard the reaction. Practically all catalysts fall into the first or positive class, but there are a few which effect what is known as *Negative Catalysis*. The phenomenon is to be observed in the case of a substance which is added to another to preserve it ; or in the oxidation of sodium sulphite, where the presence of certain organic compounds in small quantities enormously reduces the rate of attack (Bigelow). Another interesting example is to be found in the observation that ·2% moisture in pure fulminate of mercury so alters the speed of decomposition that what ought to be a detonation becomes merely an explosion (Orsman).

When carefully differentiated, however, from the paralysing effect which certain bodies exert upon positive catalysts, the importance of negative catalysis dwindles to insignificance.

(2) Unchangeableness of the Catalyst.

That the catalyst has the same chemical composition at the beginning as at the end of the reaction, is undoubtedly the most important characteristic of catalytic phenomena. Often the catalyst is known to participate directly in the reaction, but in these cases, though the equations of the intermediate stages involve the catalyst, the *gross* equation must not.

Occasionally, the catalyst is found to emerge from the reaction in an altered *physical* state. Thus, the crystalline variety of manganese dioxide, used as a catalyst in the decomposition of potassium chlorate, finishes as a fine powder, and a similar curious alteration is found in the oxide of iron employed in the Claus furnace and the platinum of the Sulphuric acid process. It appears necessary in these instances for the catalyst to mature before attaining its maximum activity, this " ageing "

consisting most probably of a physical devolution into a fineness of division greater than can be obtained by mechanical means. It must be noted, however, that the variation of energy produced by the change can hardly modify the reaction to any extent.

(3) AMOUNT OF CATALYST NECESSARY.

(a) *The Amount must be Small.*—In catalytic reactions, only a trace of the foreign material is sufficient to effect the transformation of indefinitely large quantities of the reacting substances. For example, ·0004 gr. of colloidal platinum will bring about the combination of 10 litres of hydrogen and oxygen without the activity of the catalyst being impaired (Ernst). This necessity for a mere trace of the added material constitutes one of the important characteristics of catalytic reactions.

There are instances in which the solvent, a third and unchanging body, varies the velocity of the reaction between two substances dissolved therein, and these would therefore fall within the purview of our definition, unless, as should be the case, exception were taken to them on the ground of the large amount of the third body necessary.

(b) *The Amount remains Constant.*—Unless side reactions interfere, the quantity of the catalyst remains unchanged. Of course, in practice, renewal of the catalytic agent at intervals is necessary, largely on account of deterioration consequent upon the accumulation of " poisonous " material, of which more will be mentioned later.

Instances of true catalysis, however, are known, in which the catalyst either increases or decreases in quantity as the reaction proceeds, the apparent contradiction arising from the fact that the catalyst is set free or absorbed by the reaction itself. The

phenomenon is known as *Autocatalysis*, and an example is found in the hydrolysis of an ester by water, where the liberated acid acts as the catalyst.

At this point, it is convenient to refer to the large and interesting class of chemical reactions known as *Induced Reactions*, in which a slow reaction between two substances is accelerated in the presence of a simultaneous rapid reaction between one of the reacting bodies of the first reaction and a third body. For example, a solution of sodium arsenite when shaken with air undergoes no change, whereas sodium sulphite similarly treated is rapidly oxidised. If now a mixture of sodium sulphite and sodium arsenite in solution be shaken with air, both salts are oxidised. In other words, the oxygen of the air is activated to a sufficient extent to attack sodium arsenite by the mere presence of a varying quantity of sodium sulphite. The third body, in this case sodium sulphite, therefore acts in a manner which suggests catalysis, even though its quantity throughout the reaction is a diminishing one. For a complete discussion of this class of reaction, the reader is referred to Skrabal's " Die induzierten Reaktionen " in the *Sammlung chem. und chem.-techn. Vorträge*, Bd. 13, p. 321.

The mention of other classes of reactions bordering upon the catalytic, raises the question as to the exact line of demarcation between catalytic and non-catalytic processes. As a matter of fact, it is very difficult to draw such a line. In cases of doubt, it is well to fall back upon the definition, and failing that, upon the characteristics now under discussion. The Weldon process, for instance, would be relegated to the class of *False Catalysis*, for though the lime employed apparently plays the part of a third and necessary agent, yet it becomes transformed during the process, and thereby transgresses the definition. The preparation

of nitro-glycerine, again, involves a reaction which comes even nearer the truly catalytic, since the successful nitration of glycerine certainly requires the presence of concentrated sulphuric acid, which latter emerges from the reaction chemically unchanged. The reaction might, therefore, be held to fall within the scope of our definition, but would still not be admitted to the class of true catalytic reactions by reason at least of the amount of third substance required.

(c) *Proportionality between Amount of Catalyst and the Reaction Velocity.*—As a rough generalisation, it may be stated that the activity of a catalyst is directly proportional to its concentration—a relation that would not be unexpected, seeing that the great majority of catalytic processes are monomolecular reactions. In some cases, nevertheless, the relation between the velocity constant at a particular temperature and the concentration of the catalyst is not a linear one.

(4) Incapacity of Catalyst for Starting a Reaction.

Among chemists and physicists, the question as to whether or not the catalyst is capable of starting a reaction is still a moot point. There are many who carefully differentiate catalytic reactions from what are called " trigger actions," meaning by the latter term reactions which cannot take place unless released, or their chemical forces unloosened, in some way.

This distinction will be best brought out by a mechanical analogy. Imagine a sheet of material inclined at such an angle that a weight can just slide slowly down. Now grease the bottom of the weight and the rate of fall is greatly increased. The grease then acts in an analogous manner to a catalyst, its

influence being proportional within limits to the amount of it used. If, however, the weight be held at the top of the incline by one or more catches, the rate of fall of the weight is quite independent of the number of catches, being always the same. We have then an analogy with " trigger reactions," of which the crystallisation of supersaturated solutions is a good example. The crystallisation of such a solution has been shown to be independent of the amount of crystal with which it is inoculated (Moore), and on this ground, has been refused inclusion with catalytic processes.

Difference of opinion is mainly concerned with those reactions, such as that between hydrogen and oxygen, which do not appear to take place at all under ordinary conditions unless a catalyst is present. Ostwald regards such reactions as infinitely slow under these conditions, arguing that since the reaction does take place at high temperatures, and as the velocity becomes progressively slower with diminution of temperature, it is reasonable to infer that a very slow reaction velocity could exist even at ordinary temperatures. The fact remains, nevertheless, that this velocity is too small to admit of measurement by present-day methods and apart from the above reasoning, therefore, experiment would lead us to believe that catalysts are capable of initiating reactions.

(5) Effect upon the Final State of Equilibrium.

The difference in the energy equations of the initial and final states of a reaction represents the amount of energy transformed, and since a catalyst introduces no energy, it follows that the final state of equilibrium must remain unaffected. Otherwise, of course, by permitting the reaction to take place

alternatively with and without the assistance of a catalyst, energy could be generated and a perpetual motor established.

Again, the final state of equilibrium of an inverse reaction depends only upon the ratio of the velocities of the two inverse reactions, and since this final state has been shown above to remain unaltered by the introduction of a catalyst, it may be deduced that the catalyst affects the two reaction velocities to the same extent, in order to keep their ratio constant.

As a further deduction from the same statement that the final state of equilibrium is independent of the catalyst, it may be observed that the state of equilibrium is independent of both the reaction and the quantity of the catalyst. Thus, in the case of the contact process for sulphuric acid, it is not the equilibrium, but only the velocity of its attainment which is affected by the use of vanadium pentoxide or ferric oxide instead of platinum.

(6) Effect of additional Substances upon Catalysts.

(a) *Poisons.*—It is a curious and important fact that the activity of a catalyst is liable to be greatly diminished by the presence of another substance, of which even a trace is often sufficient to paralyse the catalyst. The classical instance of such an *anti-catalyst* or *poison*, as they are called, is taken from the manufacture of sulphuric acid by the Contact process, where at the very outset it was found that the platinum asbestos employed for the oxidation of sulphur dioxide, deteriorated so quickly as to render the process unworkable. Happily, the threatened ruin of this rising industry was averted by the discovery that it was the arsenic and other impurities con-

tained in the sulphur dioxide which clogged the pores of the platinum and accounted for its diminished activity. Similarly, in the recent synthesis of ammonia by Haber the presence of poisons contributed greatly to the difficulties involved in the establishment of the process on a commercial basis.

In all cases, the effect is remarkable for the smallness of the quantity of poison required for rendering the catalyst inactive. In the last-mentioned process, for instance, the iron used as catalyst becomes quite " dead " when it contains $\frac{1}{10}\%$ sulphur, and is of little use with $\frac{1}{100}\%$ impurity even.

Arsenic seems to paralyse the action of most catalysts. The same applies more or less to prussic acid, mercuric chloride, iodine, etc., though each catalyst usually has its own list of poisons. Some of the poisons for the iron of Heber's synthesis, for instance, are of quite a different nature from those of the platinum in the sulphuric acid manufacture. In some cases, especially when the inhibitor is oxidisable, the catalyst may recover its activity ; in the remaining cases, the catalyst must either be discarded or its paralysis prevented by careful purification of the reacting materials.

Enzymes, which are also catalysts, are subject to a similar inhibiting influence, often by the same substances that poison purely " inorganic " catalysts. The phenomenon is to be observed also in blood catalysis, where the antitoxins oppose the destructive effect of the toxins upon the blood.

The action of catalytic poisons should not be confused with that of negative catalysts. In the latter case it is the reaction which is retarded, whereas in the former the catalyst has its activity reduced.

(b) *Promoters*.—In contradistinction to the above-

mentioned inhibiting substances, it has recently been discovered that there are other substances which, when added in minute quantity to a catalyst, *increase* its activity. Thus, practically all metallic catalysts become activated when certain oxides or compounds or other metals are distributed through them. In Haber's synthetic ammonia manufacture, for instance, the iron, platinum, osmium or uranium employed as catalyst is quickened to an enormous extent by the presence of traces of the salts of other metals or, with certain exceptions, of the other metals themselves. Further research in connection with these *promoters*, as they are called, would be amply repaid.

When the additional substance does not catalyse the main reaction, but rather the production of the catalyst, the phenomenon has been referred to as *Pseudo-catalysis*. A technical example is furnished by the drying of linseed-oil, where the addition of the so-called siccative, such as the oxides of manganese, lead or zinc, is found to hasten the process, probably by accelerating the development of the peroxide-like compounds which determine the drying (Genthe).

It may be noticed here that the joint effect of two catalysts need not necessarily be the sum of the effects of each catalyst taken separately. Though this does sometimes hold, the joint effect is more often greater and only occasionally less.

(7) Specific Activity of Catalysts.

As Ostwald has pointed out, there is probably no kind of chemical reaction which cannot be influenced catalytically, and no substance which cannot act as a catalyst. Yet each reaction requires its own specific catalyst or catalysts. True, under Armstrong's theory, water or some other electrolyte

is essential to all chemical reactions, but experiment is against this generalisation. There are, moreover, particular catalysts, such as platinum and nickel, which appear capable of manifold application and theory has speculated much upon their *modus operandi*, but in point of fact, no general method is available by which guidance is offered in the selection of a suitable catalyst for a given reaction. Occasionally, the discovery of such a body is a matter of accident or good fortune, as in the case of the manufacture of artificial indigo, where the accidental breakage of a thermometer liberated the catalyst which rendered practicable the most obstinate reaction of the process. More generally, however, before the commercial success of a catalytic process is assured, years of systematic scientific research with all manner of likely catalysts are involved.

CLASSIFICATION.

For the purpose of convenience, catalytic agents may be broadly divided into three classes :—

(1) Chemical agents, which function by means of intermediate reactions. The so-called *carriers* fall into this class, as well as the catalysts of what are known as " cyclic actions."

(2) Physical agents, such as finely-divided materials in general, hot and cold surfaces, etc., in which the effect is dependent upon surface tension, occlusion, diffusion, or other physical phenomena.

(3) Indeterminates, which appear to combine more or less the above two functions. Enzymes probably fall into this division.

A classification of this kind is naturally only a provisional one, for it is not certain in many cases how the catalyst does function. Indeed, there is

good reason for believing that all of them exert their influence by participating in the reaction, in which case only the first section would survive. But this classification is as good as our present ignorance of the theory of catalytic action permits, and will require revision only after much further investigation has been made and many more results accumulated.

CHAPTER II.

Sulphuric Acid Manufacture.

As examples of the application of catalysis to industrial chemistry, the two methods for the manufacture of sulphuric acid deserve first mention —the Chamber process as an illustration of the first class of catalytic action, and the Contact process as illustrative of the second.

In each case the atmospheric oxidation of sulphuric dioxide is the primary reaction involved. Now, at ordinary temperatures, and then only in solution, sulphur dioxide is oxidised with extreme slowness, while even at the temperatures which obtain during the roasting of pyrites, the reaction only takes place to a small extent. For accelerating the oxidation two separate methods are available, corresponding to the two processes above mentioned : the first based upon the capacity of oxides of nitrogen to serve as " carriers " of atmospheric oxygen to sulphur dioxide in the presence of water, and the second upon the property of platinum and other " contact " bodies to induce in the gaseous state the rapid formation of sulphuric anhydride. Each of these methods will be dealt with from the catalytic point of view.

I. Chamber Process.

The oxides of nitrogen function as true catalysts for this process, since the greater part of them can be recovered unchanged from the products of the reaction and utilised repeatedly for accelerating the

oxidation of further quantities of sulphur dioxide. Consequently, a modern Chamber plant includes arrangements both for recovering the nitrogen oxides from the exit gases of the leaden chambers in which the oxidation of the sulphur dioxide has taken place and for reintroducing the same into the apparatus again.

The cycle of operations is briefly this : The hot gases from the pyrites burners, containing about 7% sulphur dioxide, are made to take up oxides of nitrogen by being brought into contact in a Glover tower with a solution of nitrosyl sulphuric acid, *i.e.*, sulphuric acid which has absorbed the nitrogen oxides of a previous operation. The gaseous mixture is then passed through a series of leaden chambers, into which steam is forced or dilute sulphuric acid sprayed, for the completion of the reaction and the deposition of the resulting acid. Incidentally, it should be noticed that about 15% of the total acid is produced in the Glover tower itself, the remainder in the chambers. After playing their catalytic *rôle*, the nitrous gases emerging from the last chamber are absorbed by sulphuric acid in a Gay-Lussac tower forming nitrous vitriol, which is transferred to the Glover tower for the introduction of its contained nitrous gases into fresh burner mixture.

In the most carefully conducted systems, however, a loss of nitrous fumes occurs, and this has to be made good, usually by the periodic addition of nitric acid at some point of the cycle. The English method is to introduce an iron pot containing nitre and sulphuric acid into the burner gas flue, whilst on the Continent it is the practice to add liquid nitric acid to the nitrous vitriol of the Glover tower. The nitric acid is employed as a convenient means for introducing the nitrous gases and does not itself function as the catalytic agent.

As to what is the real catalyst, many divergent opinions have been put forward. I have elsewhere* briefly outlined the more important theories, and it is not necessary therefore to reopen the discussion here. Many nitrogen complexes, apparently easily interchangeable, are formed by the interaction of nitrogen oxides, sulphuric acid, water and oxygen, and though, for the sake of convenience, nitric oxide may be referred to as the catalyst it is probably one of the above-mentioned bodies which really functions in this way. The various theories advanced by Lunge, Raschig, Divers and others, differ from each other chiefly in their conception of the intermediate compound or compounds.

There is no question, however, that the reaction proceeds in any other way than by means of "intermediate reactions." These reactions have already been referred to, and later on a general discussion will be undertaken in the light of their bearing upon the explanation of catalytic action. At this stage it is only desirable to mention that the influence of a catalyst meets with some explanation if it can be shown that one or more intermediate compounds are transitorily produced, whose formation and decomposition proceeds more rapidly than the direct reaction. In the present case, taking a simple view of the reactions involved, the instantaneous formation of "chamber crystals" from sulphur dioxide, nitrous vapours and oxygen provides a common lecture experiment, as also the equally instantaneous decomposition of these crystals when brought into contact with water. By the postulation, then, of the intermediate formation of "chamber crystals," the mystery surrounding the acceleration of the normally slow reaction between sulphur dioxide, water and oxygen by the agency of nitric oxide

finds a plausible solution. Of course, the problem is not such a simple one as this ; but an explanation even on these lines would be preferable to a curt dismissal of the reaction by simply dubbing it " catalytic "—a term too often employed to cover our ignorance. Only by a careful elucidation of the intermediate reactions involved can we justify our application of this term.

With regard to the above-mentioned inevitable loss of nitrous gases, recent investigation has demonstrated that the whole of the loss, averaging 3 to 4 parts of nitre per 100 parts of sulphur burnt as pyrites, cannot be accounted for by leakage, incomplete absorption, etc. In addition to these " mechanical " losses, there appears to be a decided " chemical " loss occasioned by secondary reactions, probably comprising the reduction of the active oxides of nitrogen to the inactive nitrous oxide, nitrogen, or even ammonia. The extent of the reduction, however, is still a matter of controversy.

The Chamber process is an old-established one, but with the aid of modern developments, such as Falding's high chambers and Opl towers, it is still able to compete successfully with the rival Contact method.

II. Contact Process.

The catalytic activity of platinum in promoting the union of sulphur dioxide and oxygen was observed as long ago as 1831 by Phillips, but its successful utilisation upon an industrial basis is a matter only of comparatively recent years. The protracted development is accounted for by the many difficulties encountered, difficulties arising largely from the inadequacy of contemporary engineering chemistry. Now that these obstacles have been overcome, full technical success is assured and the process bids fair ultimately to oust the
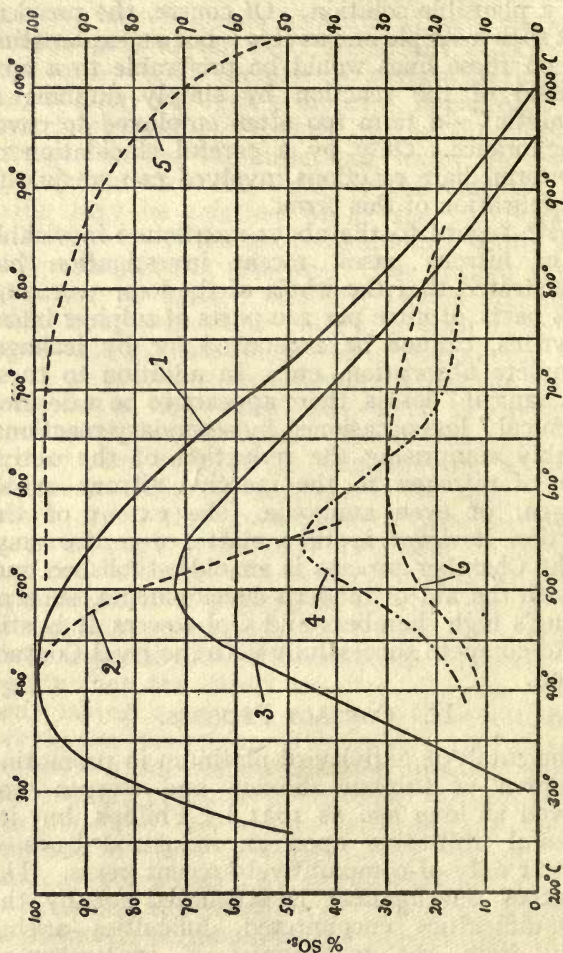
FIG. I.—TEMPERATURE OF REACTION.

older Chamber process, at least in the manufacture of the more concentrated acid.

The most serious difficulties in the successful

working of the process were concerned with the regulation of the temperature and the gradual destruction of the catalytic power of the platinum.

The reaction—

$$SO_2 + O = SO_3$$
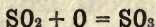
is accompanied by the evolution of 32,200 calories, a quantity sufficient to damage irreparably the contact material unless precautions are taken. Of course, with the diluted burner gas mixture— and the law of mass action demands an excess of oxygen—the effect of the heat developed is not so great, though it is still enough to raise the temperature above that for obtaining the best results.

The influence of the temperature upon the reaction, together with other relations, was investigated by Knietsch, of the Badische Anilin u. Soda Fabrik, and his results in this connection, published in 1901, are indicated by Figs. 1 and 2. Technical burner gas, containing 7% sulphur dioxide, 10% oxygen, and the rest nitrogen, was passed at various rates over platinised asbestos heated to different temperatures, and it was observed (see curve 1, Fig. 1) that the reaction began at about 200° C. and reached approximate completion at 420°, whilst above this temperature the yield of sulphuric anhydride gradually fell off until at 1000° no reaction was possible. By increasing the rate of flow, the temperature of maximum conversion increases, but at the same time, the maximum yield diminishes. This is clearly shown by curve 2, Fig. 1, which traces the loci of the maximum for the curves representing faster rates of flow. Curve 3, Fig. 1, is an example of such a curve, the speed in this case being 100 times as fast as that involved in curve 1.

In Fig. 2, the influence of the temperature upon the reaction is plotted against the rate of flow of

the gases, or what amounts to the same thing, the quantity of platinum employed.

From these curves, it is evident that, with platinum as the catalytic agent, the most desirable temperature lies at about 420° C. A higher temperature would increase the velocity of formation of sulphur trioxide, but at the same time detrimentally affect the equilibrium, so that a compromise is usually effected at, or somewhat above, 450°. The most suitable temperature depends, of course, upon several factors, such as the percentage of the constituents of the gas, the quantity passing through, the efficiency of the contact material, etc.

However, to maintain the contact mass at the desired temperature, some cooling is necessary, and this is generally brought about by causing the whole or part of the burner gases to pass through pipes surrounding the converter, whereby the entering gases are pre-heated to about 300°. Superheating at the beginning of the reaction is avoided, either by bringing the burner gases into contact with material of gradually increasing richness in platinum, or by effecting the reaction in separate stages in different converters, the sulphuric anhydride contained in the gases leaving the first converter being absorbed before passing the gases into the second.

The remaining difficulty, that of the gradual diminution in the efficacy of the platinum employed, is one which has troubled manufacturers from the very beginning. As before, the cause of the diminution was located by the researches of the Badische firm, and found to reside in the accumulation in the contact material of " poisonous " substances arising from the impurities contained in the burner gases. In Chapter I. it was mentioned that mere traces of these " poisons " act detrimentally to the activity of the catalyst, and contact

platinum is a case in point, for the presence of 1 to 2% of arsenic compounds was found to render it completely inactive. In addition to moisture, crude burner gases contain both gaseous and suspended impurities, chief among which are compounds of arsenic, antimony, phosphorus, selenium, mercury, and lead. The presence of a trace of water, however, was found to be essential to the reaction, though in greater quantities water had a deleterious effect.

To remove objection on this ground to the use of platinum as contact material, the burner gases are subjected to purification before being introduced into the converter. This is a simple matter as regards the greater quantity of impurities present in the gases, but unfortunately the last traces are found to resist removal very tenaciously. In a modern plant, purification is effected by first treating the gases leaving the burners with a jet of steam, then by cooling and washing, and finally by passage through sulphuric acid to remove all water but that sufficient to promulgate the reaction. Optical and chemical examination should then indicate complete absence of impurity. It has been suggested, as an alternative, to first condense or compress the burner gases and then allow them to expand in the presence of porous material, when the impurities are stated to remain behind.

Owing to the cost of purification, as well as to the high price of platinum, the use of other contact material is now finding application. Ferric oxide appears to be the most promising of these, for, apart from its cheapness, which permits of repeated replacement, its activity is not liable to the same degree of diminution as platinum. Arsenic compounds, for instance, combine with it to form a nonvolatile compound which only slowly reduces the activity. Moisture appears to have the most
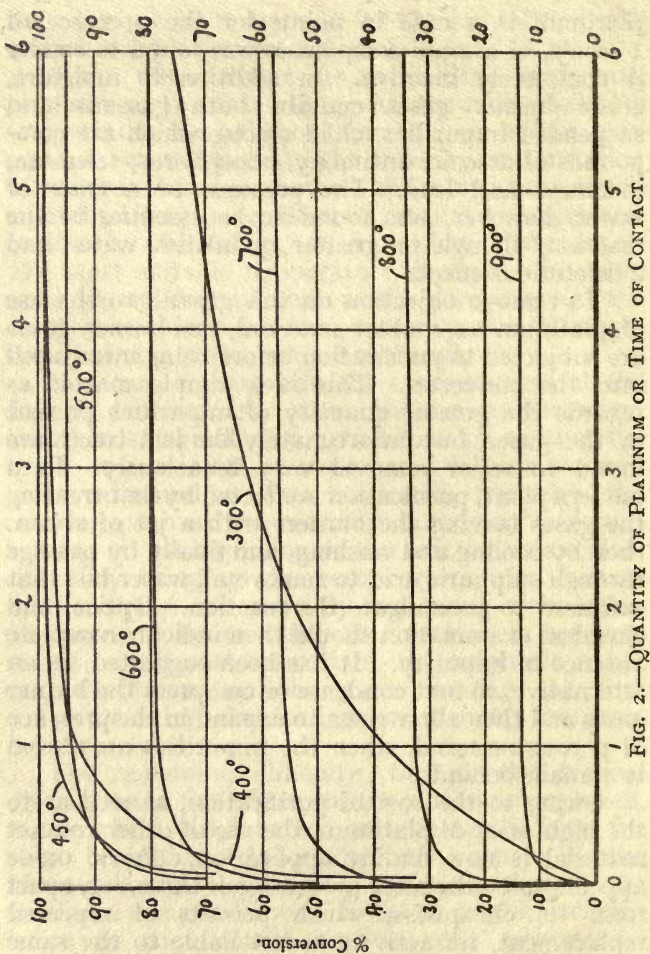
FIG. 2.—QUANTITY OF PLATINUM OR TIME OF CONTACT.

deleterious effect, and the burner gases are therefore just dried before being introduced into the converter. It might be noticed that arsenic pentoxide, free from

iron, itself possesses good catalytic powers for this reaction.

The great disadvantage of ferric oxide lies in the fact that quantitative conversion of sulphur dioxide into sulphuric anhydride cannot be obtained by its aid. This is brought out by curve 4, Fig. 1, which represents the yields obtainable at various temperatures when pyrites cinders were employed as contact agent. From this curve, it will be seen that the maximum conversion does not quite attain 50% (under modern conditions the yield does not rise much above 60%), and then at a temperature over a hundred degrees higher than is requisite for platinum as contact material. The fact that the optimum temperature for ferric oxide is higher than for platinum is really no disadvantage, because at the higher temperature the reaction velocity is far greater, and this allows of a more rapid production of sulphur trioxide. Ferric oxide, therefore, finds its proper sphere of usefulness when employed in conjunction with platinum, the former being used for the first stage of the operation at high temperatures and, after absorption of the resulting sulphur trioxide, employing the latter to complete the reaction at a lower temperature.

Incidentally, attention is drawn to curve 5, Fig. 1, which shows the effect of heat upon sulphuric anhydride in an empty porcelain tube, *i.e.*, out of contact with the catalytic material. The remarkable deduction can be drawn from it that sulphuric anhydride, once formed, is very stable at quite high temperatures when contact substances are absent. Complete dissociation is only obtained at 1200° C. Curve 6 summarises the results when pieces of porcelain were employed as the contact material.

Investigators have been busy, in recent years, seeking still other catalysts for the Contact process, and with considerable success. Thus, besides ferric

oxide, vanadic and tungstic oxides are found to be available, as also the sulphates of nickel and cobalt. In addition, the oxides and sulphates of chromium, manganese, uranium and copper ; the oxides of aluminium, zinc, and particularly of the rare metals ; natural and artificial porous material, usually incorporating finely-divided platinum ; are numbered amongst the list of catalysts, and of late years, many patents have been taken out pertaining to these. Indeed, the discovery of a catalyst of some sort appears to be an easy matter. So far as is known, however—and most factories maintain great secrecy upon this and similar points—platinum in the form of platinised asbestos, and ferric oxide as pyrites cinders, the former the material first to be employed and the latter introduced but a few years later, remain the only catalysts in practical use.

With regard to the theory of this reaction, but little can be said. Platinum is usually regarded as belonging to the second class of catalyst, viz., those which exert their influence by reason of the occlusion, or condensation upon their surface, of the reacting gases. Some doubt, however, as to the correctness of this belief is raised by a consideration of the numerous other catalysts above referred to, for many are seen to be oxides or sulphates of metals of dual valency whose action depends upon the reduction of the higher form of oxidation at the same time as the lower is oxidised. Ferric oxide, of course, certainly belongs to this class. Moreover, an hypothetical platinum dioxide (Engler and Wöhler) has for some time been regarded by a few as the transitory intermediate product, whilst the ordinary monoxide is also said to possess strong oxidising powers (Wöhler). The majority of chemists, nevertheless, arguing from the well-authenticated influence of the fineness of division of a substance upon the acceleration of a reaction,

prefer to regard the action of platinum, at least, as being more physical than chemical. In any case, further research on this point is needed.

Quite recently (1912), a new theory of the catalytic action of platinum in this reaction has been put forward by Wieland. It has been mentioned that the absolutely dry mixture refuses to combine under the influence of platinum, and on this fact Wieland bases his hypothesis. The platinum, in opposition to the ordinary assumption, does not then cause the combination of sulphur dioxide and oxygen, but simply promotes the combination of oxygen with hydrogen which is liberated during the reaction, the resulting water being then reintroduced into the cycle. The equations—

$$SO_2 + H_2O \longrightarrow H_2SO_3$$
$$H_2SO_3 \longrightarrow SO_3 + H_2$$
$$H_2 + O \longrightarrow H_2O$$
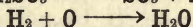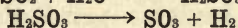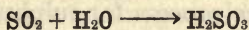
then represent the stages of the reaction.

CHAPTER III.

INDUSTRIAL CHLORINE, SALT-CAKE, AND SULPHUR RECOVERY.

BEFORE proceeding to a discussion of the newer applications of catalysis to inorganic processes, reference must be made to several other industries which, although well known, possess great interest when viewed from our present standpoint. The most important are the Deacon process for chlorine, the Hargreaves-Robinson process for salt-cake, and the Claus-Chance process for sulphur recovery from alkali waste.

I. DEACON PROCESS.

For close upon three-quarters of a century, it has been known that a mixture of hydrochloric acid gas and oxygen, when strongly heated and particularly when in contact with porous substances, undergoes partial decomposition, with the formation of water and the liberation of chlorine (Oxland, 1845).

$$2HCl + O = H_2O + Cl_2.$$

Under the stated conditions, though, the yield is so small as to render the process impracticable ; but it was soon discovered that by the employment of some substance capable of acting as an oxygen carrier, the decomposition could be greatly assisted. Of such substances the salts of copper have been found most useful, especially the chloride, which was first employed by Vogel in 1855 in a method involving successive combination with hydrochloric acid, and decomposition by oxygen. Like that of

Oxland's, however, this process proved unsatisfactory though for a different reason. It remained for Deacon and Hurter in 1868 to establish a successful chlorine manufacture on these lines by the employment as catalyst of pumice impregnated with cupric chloride, thereby combining the efficiency, so far as the yield was concerned, of Vogel's method with the continuity of Oxland's.

In the course of a series of investigations it was established by Hurter that the cheapest and most efficient catalyst available for the purpose was cupric chloride, and, strangely enough, this contact material still holds the field against all others that have been proposed since that time. This result was deduced from a diagram showing the affinity of all likely elements for oxygen, chlorine and hydrogen—the diagram being obtained by plotting the heats of combination of these compounds against the atomic weight of the element concerned—from which it could be seen at a glance that no other metal than copper forms two oxides and two chlorides in which the combination is of so loose a character. The diagram (see *Jour. Soc. Chem. Ind.*, 1883, 2, 106) is mentioned here, since it furnishes one of the few cases in which the likeliest catalyst has been selected by a preliminary theoretic inquiry.

In the early stages of the development of the process, the working results proved somewhat unsatisfactory. For some cause, as then unexplained, the catalyst was quickly rendered inactive when " roaster gas " was employed, the latter, of course, having as impurity the products of combustion from the open furnaces in which the second stage of the salt-cake process is effected. The poisonous effect of impurities upon the catalyst had not been realised at that time, so that the employment of " roaster gas " had to be abandoned and recourse

made to " pan gas," *i.e.*, the gas evolved from the closed pans during the first stage of the decomposition of salt by sulphuric acid. In thus evading the first difficulty, however, another difficulty was raised ; for whilst the efficient working of the process demands a continuously-supplied mixture of hydrochloric acid gas and air of definite composition, the evolution of gas from a salt-cake pan is such a diminishing and variable quantity that this condition cannot be fulfilled. By employing two or more salt-cake pans and suitably mixing the gases, the drawback was removed to some extent, but the compromise did not tend to efficiency.

The disadvantages attendant upon the use of " roaster gas " have been overcome largely by the researches of Hasenclever (1876). This investigator attributed the rapid deterioration of the catalyst to the presence of sulphur trioxide in the " roaster gas," whereby a coating of sulphate was formed on the copper chloride employed ; and proposed to eliminate this injurious action by first absorbing the gases in water and then treating the resulting impure acid with hot sulphuric acid and air, by which means a mixture of pure gaseous hydrochloric acid with the requisite amount of air could be obtained. Other remedies have been suggested, but Hasenclever's process (1883) is admittedly the most thorough.

As would be expected, sulphur trioxide is not the only undesirable impurity in the " roaster gas." Oxide of arsenic produces arsenate of copper, which is even less reactive than the sulphate. The presence of carbon dioxide, too, introduces difficulties, for if present as a diluent of Deacon chlorine, it militates against the production of strong bleaching powder, a serious objection when it is remembered that Deacon chlorine is largely intended for the " bleach " industry. This latter difficulty has been surmounted,

however, by improvements in construction of the apparatus whereby leakage is diminished.

Another impurity which exerts a deleterious influence is sulphur dioxide, for in the decomposer this is converted into sulphuric acid. Kolb (1891) provides for the removal of both the dioxide and trioxide of sulphur by passing the "roaster gas" over lumps of salt maintained at about 450° C., as in Hargreaves' process (see below). Both acid gases are absorbed, and by interaction with the salt, generate a little more hydrochloric acid, which passes along with the unchanged hydrochloric acid of the "roaster gas." According to Gaskell (1893), the same effect is obtained by adding to the contact mass such substances as have a greater affinity for sulphur dioxide and trioxide than copper, *e.g.*, calcium or magnesium chlorides.

Water also acts detrimentally, so that it is necessary to cool the gases down to about 40° C., and dry them with sulphuric acid before they are allowed to enter the decomposer.

It is now recognised that cupric chloride is one of the most sensitive of catalysts to "poisonous" substances. On account, therefore, of the small traces of impurities, such as the above-mentioned arsenic compounds, which it is impossible to remove, as well as by reason of a gradual volatilisation of the copper salt, it is found necessary to renew the catalytic material at regular intervals.

This is effected in a satisfactory manner by the type of decomposer shown in Fig. 3, comprising an upright iron cylinder A, within which a cylindrical ring of contact material B is supported by iron shutters C. The annular space between the shutters is divided into six compartments, each of which is emptied in succession every fortnight. The contact mass, wholly renewed in this way every three months, consists of broken brick which has been soaked

in a solution of cupric chloride, and contains when dry from 0·6 to 0·7% metallic copper. Entering by the pipe D on the circumference of the cylinder, the gases pass through the contact mass into the inner space and are led away by the pipe E.
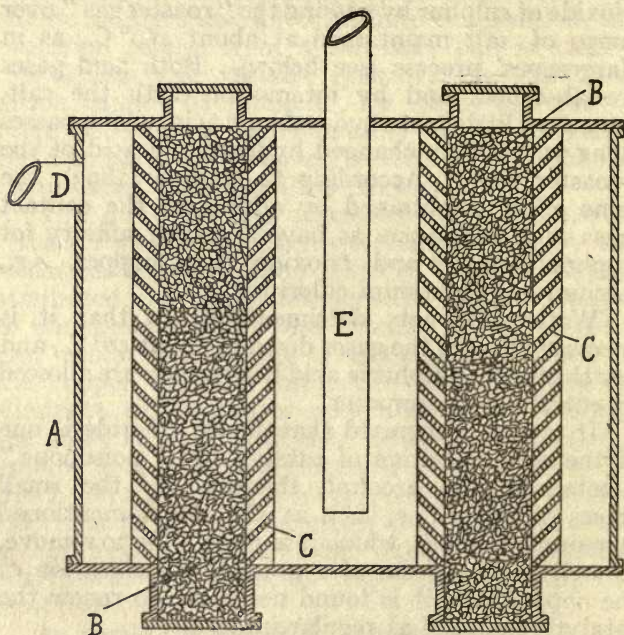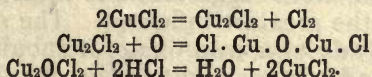

FIG. 3.—TYPE OF DECOMPOSER.

The regulation of the temperature of the reaction in the decomposer is one of the primary considerations of the process. The most suitable temperature appears to be at 450—460° C.; above this, volatilisation becomes excessive, whilst below it, the yield is much diminished.

At the temperature of the decomposer, by no

means all of the hydrochloric acid is converted into chlorine. Under the best practical conditions, only about two-thirds of this decomposition is effected, and the undecomposed acid has therefore to be recovered and applied to other purposes. Even then, however, a much greater percentage of the hydrochloric acid is utilised than in any process employing either natural or recovered manganese dioxide.

The sensitiveness of cupric chloride has naturally led investigators to seek other contact substances for the production of chlorine from gaseous hydrochloric acid. Ferric chloride was proposed by Thibierge (1855), platinised asbestos by Weldon (1871), chromic oxide by Hargreaves and Robinson (1872), pumice impregnated with nickel chloride by Mond (1886), a mixture of magnesium and manganese chlorides with magnesium sulphate by de Wilde and Reychler (1889), the chlorides of the rare earths by Ditz and Margosches (1904), and the double compounds or mixtures of cupric chloride with other chlorides by Dieffenbach (1908) ; but the application of none of these materials, so far as is known, has emerged from the experimental stage. From this incomplete list, however, it will be seen how numerous and varied are the catalysts for the interaction between air and hydrochloric acid gas.

The mechanism of the reaction is usually explained on the lines of the intermediate formation of an oxychloride of copper, $CuO \cdot CuCl_2$. The following then comprises the cycle of reactions :—

$$2CuCl_2 = Cu_2Cl_2 + Cl_2$$
$$Cu_2Cl_2 + O = Cl \cdot Cu \cdot O \cdot Cu \cdot Cl$$
$$Cu_2OCl_2 + 2HCl = H_2O + 2CuCl_2.$$

Recently, however, Levi (1905, etc.) has advanced the theory that the catalytic activity of cupric

chloride and its congeners is attributable to their hydro-avidity, *i.e.*, to the temporary formation of hydrates; for in the system $2HCl + O$, the tendency is towards the formation of water, and this would naturally be favoured by the presence of any substance capable of absorbing water. The usual catalysts of this process are certainly of this type; but, on the other hand, it is found that substances, such as calcium chloride, possessing marked hydro-affinity, exert little or no catalytic action. The results of Levi's experiments, moreover, it may be argued, can be explained just as well by the older hypothesis set out above.

II. Hargreaves-Robinson Process.

The direct process for the manufacture of salt-cake, first established on a successful practical basis by Hargreaves and Robinson in 1870, is deserving of mention in view of its later developments. Originally the process involved no catalyst, but consisted simply of the passage of pyrites gases over suitably-prepared salt at 500—550° C. in a series of chambers, giving rise to the following reaction :—

$$2NaCl + SO_2 + O + H_2O = Na_2SO_4 + 2HCl.$$
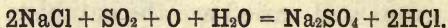
In 1886 they suggested increasing the speed of the reaction by the addition of a little ferric oxide to the salt; and again, in 1907, acquired the French rights for a process in which the reaction is promoted by the use of copper and iron salts. Other salts and oxides were suggested, but these latter appear to have the greatest influence. The superiority of copper oxide over iron oxide, it should be noticed, had already been pointed out by Krutwig and Dernoncourt in 1897, and by Conroy in 1902.

To take advantage of the catalytic activity of

the copper and iron oxides, the salt is moistened, prior to moulding, with a solution of copper or iron sulphate or both, the content varying between 0·1 and 1·0%. The upper limit is only possible when the resulting salt-cake is intended for the Leblanc soda process, for there a little impurity has no effect ; but where a purer material is required, as in the case of salt-cake for use in glass works, only a very small amount of the catalyst may be added. The addition of these materials not only increases the velocity of the interaction, but also diminishes the temperature of decomposition.

III. CLAUS-CHANCE PROCESS.

At one time, the greatest source of inconvenience to the manufacturer of alkali by the Leblanc process was attached to the disposal of the " tank-waste," *i.e.*, the insoluble residue, chiefly calcium sulphide, which remains after lixiviation of the " black ash," on account both of the space it took up and the annoyance its smell occasioned to the neighbourhood surrounding the works.

Several attempts were made to work up this by-product, all of which proved unsuccessful, until in 1887 the firm of Chance Bros., after the expenditure of much time and money, succeeded in devising a process for the recovery of most of the contained sulphur at a price permitting competition with Sicilian brimstone. Incidentally, the achievement was a fortunate one for the Leblanc process, since it has enabled the latter to compete with its younger and more vigorous rival, the Solvay ammonia-soda process.

The method is based upon that patented in 1837 by Gossage (who lost his fortune in futile endeavours to establish it on a commercial footing), and consists in decomposing the calcium sulphide

of the "tank-waste" by lime-kiln gases, followed by the incomplete combustion of the sulphuretted hydrogen thus obtained.

The main difficulties of Gossage's process were concerned with the generation of carbon dioxide and sulphuretted hydrogen in a sufficient degree of concentration. When attacking the problem later, Chance had not the first of these difficulties to contend with, for the production of air containing a large percentage of sulphur dioxide had already been worked out in connection with the manufacture of ammonia-soda, resulting in the introduction of Mond kilns which produce gas containing over 30% carbon dioxide by volume, the remainder being practically pure nitrogen. The second difficulty was finally overcome by utilising the fact that if such gas, rich in carbon dioxide, be passed into a series of chambers containing moist tank-waste, the carbon dioxide first reacts with the calcium sulphide to liberate sulphuretted hydrogen, which can then be brought into contact with fresh calcium sulphide in another chamber, where it is quickly absorbed to form calcium sulpho-hydrate,

$$CaS + H_2O + CO_2 = CaCO_3 + H_2S$$
$$CaS + H_2S = Ca(SH)_2,$$
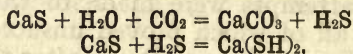
the accompanying nitrogen, meanwhile, being allowed to escape from the first chamber. If now, more carbon dioxide is admitted in sufficient quantity just to decompose the sulpho-hydrate, a highly-concentrated stream of sulphuretted hydrogen will be evolved,

$$Ca(SH)_2 + CO_2 + H_2O = CaCO_3 + H_2S.$$
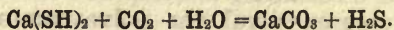
In practice, the chambers are so inter-connected as to be capable of arrangement in any required order to constitute the series. As a result, all the carbon dioxide of the incoming mixture is entirely replaced by sulphuretted hydrogen, while most of

the accompanying nitrogen is effectually eliminated. It may be mentioned that the resulting desulphurised residue is quite unobjectionable.

The sulphuretted hydrogen thus obtained is next treated with a view to the recovery of its sulphur by a process patented by Claus in 1883—originally intended, however, for other application—in which the gas, after admixture with air to obtain the desired combining proportions, is passed through a hot layer of ferric oxide.

In the usual construction of apparatus, the Claus kiln, as it is called, comprises a cylinder provided internally with a grating upon which rests a layer of broken firebrick, with a further layer of bog-iron ore superimposed. The combustible mixture, usually about 4 vols. of air to 5 vols. 38% sulphuretted hydrogen, enters at the top, passes through the porous layers, where it is burnt to sulphur vapour and steam with but little sulphur dioxide and sulphuretted hydrogen as impurity, and is drawn from the bottom into a series of condensing chambers, where part of the sulphur vapour condenses to liquid sulphur and the remainder as flowers of sulphur, along with the condensed steam.

The reaction is exothermic, so that no external heating is necessary. To start the reaction, a few shovelfuls of red-hot coal are thrown on to the oxide ; whilst the temperature is regulated by controlling the speed of the gas.

During the process the ferric oxide becomes transformed into pyrites, but the pyrites so formed has some peculiar property attached to it which ordinary pyrites does not possess, for the latter is quite useless as a catalyst.

When once the necessary temperature has been reached, the reaction is found to proceed fairly satisfactorily with other contact material, such as broken brick, though the working temperature then becomes

somewhat higher than when ferric oxide only is employed. For starting the reaction, however, ferric oxide or similar contact material must be employed ; hence the two layers in the Claus kiln. Recently it has been found that the temperature can be still further reduced by using "Weldon mud," the insoluble manganites of manganese and calcium, which are its principal constituents, serving as excellent catalysts. "Weldon mud," moreover, possesses the advantage of being able to oxidise fully the hydrogen of gases which are poor in sulphuretted hydrogen, and because of this, it too is often employed in the upper parts of the kilns. Bauxite is another material which is being used as a substitute for oxide of iron, and according to all reports, based on continued practical tests, it has proved an efficient catalyst for this process.

As mentioned when dealing with the Contact process for sulphuric acid, the catalytic activity of ferric oxide is to be attributed to the readiness of its transformation into some lower oxide when an oxidisable compound is present and its subsequent easy re-oxidation by atmospheric air.

CHAPTER IV.

FIXATION OF ATMOSPHERIC NITROGEN.

AT the present time the outstanding problem of chemical industry is concerned with the large-scale fixation of atmospheric nitrogen. It is only a few years ago that attention was drawn by several chemists of eminence to the possibility of the exhaustion of Chili nitrate, our largest natural store of combined nitrogen, at a not far-distant date ; and their warning has proved effective, for since that time, attempts to replace the natural material by artificial products have been very numerous. The few that have materialised industrially involve four distinct methods :—

(1) The direct oxidation of air by means of the electric arc to form nitrous oxides, which are subsequently converted into nitrates ; as in the processes of Birkeland and Eyde, Schönherr and Pauling.

(2) The high-temperature fixation of nitrogen to metals and metalloids, followed, if necessary, by decomposition of the resulting compounds ; as in Serpek's process, the Frank and Caro process, and the several processes of the Badische Anilin u. Soda Fabrik.

(3) The synthesis of ammonia, which forms the basis of Haber's process ; and

(4) The oxidation to nitric acid of ammonia, obtained preferably by the decomposition of the compounds produced by method (2), by a process associated with the name of Ostwald.

Of the above, the processes which depend

primarily upon catalytic phenomena are those of Haber and Ostwald, and these two will, therefore, be discussed, together with Serpek's process, which has some interest catalytically.

I. HABER'S PROCESS.

The affinity of nitrogen for hydrogen, even at high temperatures or under the influence of spark or silent discharge, is so slight as to be almost negligible. Under the influence of a catalyst, too, the smallness of the yield was formerly considered to hold out no prospect of commercial advantage. This was shown in 1881 by Johnson, who used platinised asbestos and obtained only traces of ammonia, a result which even then was not borne out by later experiments. Perman, twenty years after, could detect only minute quantities of ammonia after passing a mixture of nitrogen and hydrogen over red-hot iron and other bodies.

In 1904 Haber undertook the investigation of the ammonia equilibrium, using modern physico-chemical methods. Nernst, in 1907, communicated the results of experiments on similar lines. Both agreed that at 1,000° C. the decomposition of ammonia into its elements is almost quantitative ; which is to say that, under the same conditions, merely traces of ammonia would be formed. At lower temperatures than 1,000° C., the activity of the catalysts employed sank so low as to render them unworkable.

Undismayed by these unpromising results, Haber conducted further experiments, with the assistance of the Badische Anilin u. Soda Fabrik, in which was utilised the thermodynamical fact that pressure shifts the equilibrium of such a mixture of two reacting gases in the direction of further combination. From the results of the experiments he was able to show, in 1908, that the production of

ammonia is possible on a practical scale if the mixture of nitrogen and hydrogen be kept under a
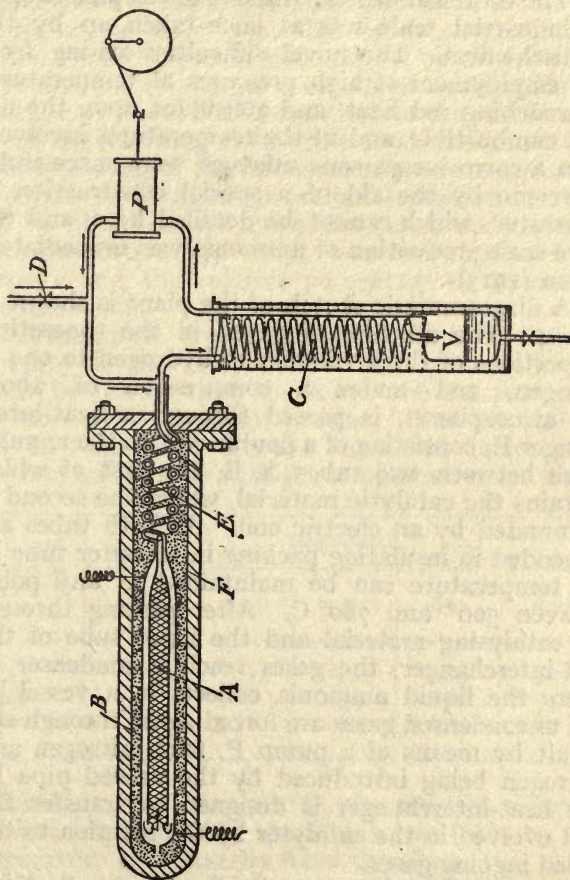

FIG. 4.—HABER'S APPARATUS.

constant high pressure during the whole of an operation in which the gases are alternately subjected to the catalytic activity of various materials,

and then freed from ammonia by absorption or condensation at a lower temperature.

The establishment of Haber's development upon an industrial scale was at once taken up by the Badische firm. The novel difficulties arising from the employment of high pressures at temperatures approaching red heat, and attendant upon the use of a combustible, and at the temperatures involved, even a corrosive gaseous mixture, were successfully overcome by the aid of a special construction of apparatus, which cannot be detailed here, and the large-scale production of ammonia was immediately begun (1913).

A diagrammatic sketch of the plant is shown in Fig. 4. The mixture of gases, in the theoretical proportions of three volumes of hydrogen to one of nitrogen, and under a compression of about 150 atmospheres, is passed through a heat-interchanger E, consisting of a double coil, to the annular space between two tubes A, B, the first of which contains the catalytic material, whilst the second is surrounded by an electric coil. As both tubes are embedded in insulating packing in an outer tube F, the temperature can be maintained at any point between 500° and 700° C. After passing through the catalysing material and the inner tube of the heat-interchanger, the gases reach a condenser C, where the liquid ammonia collects in a vessel V. The uncondensed gases are forced again through the circuit by means of a pump P, fresh nitrogen and hydrogen being introduced by the valved pipe D. The heat-interchanger is designed to transfer the heat evolved in the catalyser by the reaction to the cooled ingoing gases.

The very high pressures involved naturally limit the space that may be filled with contact material. However, at 200 atmospheres and a temperature of 650—700° C., a yield of 250 gms. of ammonia per

litre of contact space per hour is readily obtained, using pure iron as the catalyst, and passing the gases through at a speed of 250 litres per hour.

Returning now from this brief glance at the finished process, consideration must be given to the large amount of pioneer work which enabled Haber to define *a priori* all the conditions of the problem.

In the following table are embodied some of his results relating to the influence of pressure upon the ammonia equilibrium at various temperatures. It will be observed, on inspection, that an approximate proportionality exists between the working pressure and the relative percentage of ammonia in equilibrium.

Furthermore, from the fact that the yield increases as the temperature falls, the conclusion might be drawn that the lower the temperature, the more practicable the process. But there must also be taken into account the rapid decrease in the reaction velocity with the temperature, and since

Pressure (in atmospheres).	Temperature C.				
	550	650	750	850	950
1	·077	·032	·016	·009	·005
100	6·7	3·02	1·54	·874	·542
200	11·9	5·71	2·99	1·68	1·07

at values much below 500° C., the reaction velocity becomes impracticably small, a lower limit to the temperature is arbitrarily fixed thereby.

Another factor which goes still further towards defining the minimum temperature is inherent in the catalysts themselves. The catalysts first worked with, such as iron, manganese, chromium and

nickel, required comparatively high temperatures for the development of their activity ; but as the number of catalysts increased, others became available, such as osmium and uranium, which display great activity within a temperature range of 500—700° C. These temperatures now furnish the limits for practical working.

Under no circumstances, it will be noticed, are the yields so high as to render it remunerative to allow the residual gases to escape into the atmosphere after the reaction products have been removed, and it is for this reason that a continuous process has been adopted.

With regard to the rate of flow of the gases, experiments have shown that while the ammonia concentration decreases as the rate of flow increases, other conditions being unaltered, the product of the concentration and the rate of flow, which is a measure of the amount of ammonia produced in unit time, actually rises and to no inconsiderable extent. A premium is thus placed upon a rapid circulation.

Recognising the importance that is attached to the catalytic function, the Badische firm has made a very minute investigation into the relative efficiencies of various materials and the effect of extraneous bodies upon their activity. The results in these directions are of first-rate importance.

The most favourable catalysts appear to be metallic osmium and uranium carbide. The former is ruled out of consideration for industrial application by reason of its rarity and costliness, whilst the second suffers from the disability that water must be most rigorously excluded from the reacting gases. Now, as we shall see in a later chapter, gaseous combination is dependent upon the presence of a trace of moisture. The dessication of the gases must not therefore be carried as far as is desirable for the well-being of the catalyst, with the result that

the irreducible oxide is formed and the material suffers continual depreciation.

Judging by the most recent patents, pure iron is the catalyst generally employed in this process. Using this material and with the aid of various minor improvements, it has now been found possible to lower the working pressure to the neighbourhood of 50 atmospheres. In all cases it is essential, in the interests of efficiency, that the catalyst be prepared at a temperature not greatly exceeding 600° C.

Of the remaining substances which catalyse the reaction, and they are many, the most interesting are molybdenum and molybdates, tungsten and its alloys, and cerium with its congeners. Platinum, on the other hand, though related to osmium, possesses but a slight catalytic activity.

The most important feature attached to the investigation of the Badische firm was the discovery that the activity of the catalysts can be increased by the addition of certain foreign bodies. These "promoters," as they have been called in Chapter I., include various metals, the oxides, hydroxides and salts of the alkali and alkaline earth metals, as well as many other substances of the most varied nature. In many cases just a trace of the contaminating body considerably enhances the activity of the catalyst. Moreover, all the catalysts appear to possess the capacity for invigoration.

The manner in which the foreign material increases the catalytic activity is not easily explained. Most of the catalysts appear to function by participating in the reaction, *i.e.*, by the formation of readily reducible nitrides, and the promoters may then either confer a kind of skeleton formation upon the catalyst, thereby maintaining a large surface area, or in some as yet unknown way may diminish the chemical resistance of the reaction taking place on the surface of the catalyst.

Of course, contamination with certain substances has to be carefully avoided. As in the case of the contact reactions previously considered, there exist bodies which, even when present in the smallest traces, act as poisons to the catalyst. In the present instance, the great trouble occasioned by them necessitated a minute study of the influence of all possible impurities. Examples of bodies acting deleteriously are to be found in sulphur, selenium, tellurium, phosphorus, arsenic, boron and their compounds ; as also many carbon compounds ; and certain metals of low melting-point, which can be readily obtained by reduction from their compounds, but are not themselves catalysts. Lead, zinc, bismuth and tin are to be avoided, too. Such minute quantities of any of the above-mentioned as are to be found almost always in the purest commercial products and so-called pure gases are sufficient to diminish very seriously the catalytic activity. In Chapter I., for instance, it is mentioned that an impurity of $\frac{1}{100}\%$ sulphur in iron renders it nearly useless.

In view of these facts, every care is taken both to obtain pure contact material and to free the reacting gases from all poisonous bodies. The first is a comparatively easy matter, the ordinary methods of purification of course being employed. But the continuous removal of contact poisons from the reacting gases is a more difficult undertaking, particularly as chemical contingencies have brought about the replacement of the electrolytic hydrogen formerly employed by the impure hydrogen obtained from coal. This latter method of production depends upon the separation by liquefaction of the constituents of water-gas, hydrogen and carbon monoxide. Traces of carbon monoxide have then to be eliminated, together with the gaseous impurities derived from the coal decomposition, as well as the

contaminations arising from the use of piping, lubricating oil in the pumps, etc. A development of this process of hydrogen production has recently been patented, in which carbon monoxide and steam are caused to interact under pressure at 300—600° C., in the pressure of a catalyst such as iron, nickel and the like, thereby producing carbon dioxide and hydrogen, of which the former is removed by absorption, leaving hydrogen ready compressed for the ammonia synthesis. The nitrogen employed is usually obtained by the fractionation of liquid air.

In general, the gases are filtered, washed, and then conducted over various solid absorption agents, whilst in some cases further purification is effected by passage over a portion of the same material as is employed as catalyst, at a raised temperature, before introduction into the catalyser. This material is renewed repeatedly. The yield is found to be increased if both gases are deprived of water and of substances capable of producing water.

Recently the original process has been modified by passing nitrogen and hydrogen *alternately* instead of *simultaneously* over the contact substance. Under these circumstances extremely good yields result if the nitrogen be mixed previously with a small proportion (1—3%) of hydrogen. The same happens in the ordinary process if the compressed gases be allowed to expand after leaving the catalyser.

II. Ostwald's Process.

Though Kuhlmann, in 1830, observed that ammonia is oxidisable to nitric acid in the presence of platinum, the fact remained without commercial significance until within the last decade.

Ostwald and Brauer, however, in 1900, began an investigation into this reaction, and contrary to

expectation, found it so practicable that, after thoroughly testing their process, a full-sized plant was laid down some six years ago, and with such success, that several other similar works are now in course of construction.

Taking, for the time being, the following equation as representing the course of the reaction between ammonia and oxygen,

$$NH_3 + 4O = HNO_3 + H_2O,$$
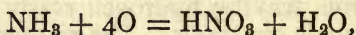
attention must first be drawn to the fact that the oxidation is incomplete, for free nitrogen would be the final product of the complete combustion. In other words, the reaction represented above is not an *ultimate* one, but instead, one involving the formation of an *intermediate* product.

Now finely-divided platinum, the best catalyst from the point of view of nitric acid formation, was found to be an excellent catalyst for the ultimate reaction also, and the problem arose as to the differentiation of these two concurrent reactions and the suppression of free nitrogen production. Fortunately, it was discovered that the former reaction takes place very much more quickly than the latter, so that if the mixture of ammonia and air be passed at a high speed through the plug of platinum forming the catalyst, high yields of nitric acid are obtainable. A further means towards this end consists of the use of smooth platinum, partly or wholly covered with the spongy or black variety. In this way mean yields of 85% conversion of ammonia into nitric acid are stated to result.

The mixture of ammonia and air found to be most advantageous in practice contains a large excess of air, having generally the proportions of one volume of ammonia to ten or more volumes of air, and such a mixture is passed over the catalyst, usually only some 1 or 2 cms. in length and

maintained at a temperature exceeding 300° C., at a velocity of from 1 to 5 metres per second. In any case, the speed of circulation of the reacting gases and the length of the catalyst should be so arranged as to give a time of contact not less than $\frac{1}{100}$ second.

The difficulty of maintaining the contact temperature at anything like a constant value with such high gaseous speeds is overcome by heating the gases entering the catalyser at the expense of the hot products issuing therefrom.

The plant for this process comprises apparatus for producing ammonia gas, catalysers for the actual reaction, and condensers for the removal of the products.

Crude gas liquor furnished the source of the ammonia first employed, the liquor being brought into contact with hot air on the counter-current principle. The resulting mixture was purified by washing and passage over milk of lime to remove carbon dioxide and sulphuretted hydrogen. In some cases no purification was effected, the products of the combustion of sulphur compounds being easily removed from the nitric acid by a single operation, while those arising from nitrogen compounds, such as aniline, pyridine, and prussic acid, themselves form nitric acid.

Recently, however, the Ostwald process has been combined with that of Frank and Caro, and the ammonia is then obtained by decomposition of calcium cyanamide with steam.

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3.$$
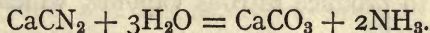
As organic materials are not found to exert any deleterious influence upon the catalyst, no purification is resorted to. The catalyst is contained in a series of stoneware cylinders, so arranged that any one of them may be put out of action without

disturbing the remainder. Stoneware is essential, since no other material is available which could withstand nitric acid vapours at the high temperatures involved, these latter usually corresponding to some value between dark and red heat.

In practice, platinum appears to be the sole catalyst employed. Other members of the same group are also reactive, though not to the same extent. Ostwald states, too, that the peroxides of lead and manganese are important as catalysts, as also the oxides of silver, copper, iron, chromium, nickel and cobalt—in fact, the oxides of heavy metals in general. Matignon has shown that glucinum, tungsten and zinc possess considerable activity ; whilst Frank and Caro have recently put forward thorium oxide and mixtures of this with other rare earth oxides as forming efficient catalysts.

The fact that peroxides and many oxides of bivalent metals possess catalytic activity seems to favour the idea that the oxygen of the reacting mixture enters into combination with the catalyst as a preliminary to the decomposition of the ammonia. To bring platinum into line with these is to presuppose the formation of the oxides, hypothetical and otherwise, mentioned in Chapter II.

The reaction involved is really not that represented above, but one in which nitric oxide is first produced.

$$2NH_3 + 5O = 2NO + 3H_2O.$$
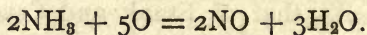
The nitric oxide reacts afterwards with the excess of oxygen to produce nitrous vapours, which dissolve to nitric acid.

The resulting acid may be neutralised by more ammonia to form ammonium nitrate, or other nitrates may be produced and put on the market as such. As the company, the Nitrogen Products and Carbide Co., now engaged in working this process

expect at some future time to have an annual output of nitrogen amounting nearly to the whole natural supply, the fear of any shortage of fertiliser, nitrates for explosives, etc., is now dispelled.

It is interesting to learn that works may be erected in England for the manufacture of nitrates for explosives, large quantities of cyanamide being stored here for the purpose. If in the last resort the stores become depleted, it will always be possible to fall back upon the sources of ammonia first utilised, viz., the ammoniacal liquors from coke ovens, blast furnaces and gasworks.

III. Serpek Process.

Before leaving the subject of nitrogen fixation, a glance must be given at this process, on account of a recent development in the direction of the catalytic. In its latest form, the process consists simply of heating a mixture of bauxite and carbon in a current of nitrogen under pressure to about 1,800° C. in a specially-designed revolving electric furnace.

$$Al_2O_3 + 3C + 2N = 2AlN + 3CO.$$
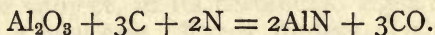
The resulting aluminium nitride is then decomposed by alkali, yielding ammonia and sodium aluminate.

$$AlN + 3NaOH = NH_3 + Na_3AlO_3.$$
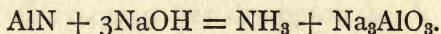
Originally, aluminium carbide was employed for the absorption, and this, again, was replaced later by alumina and carbon. In both cases the absorption of nitrogen was stated by Serpek to be facilitated by the presence of a little sulphur dioxide or hydrochloric acid gas in the nitrogen. This, however, has been disproved by recent independent investigation (1912, Tucker and Read).

Moreover, the pure alumina was found to react very slightly with carbon to produce the nitride, and Serpek therefore added a trace of metal, such as iron or copper, capable of forming an alloy with aluminium, in order to increase the production. Later research has verified this result and has further demonstrated that the impure mineral alumina, bauxite, contains sufficient catalyst as impurity, chiefly of a ferruginous nature, to render its use of great advantage.

The reaction is accelerated, too, by the presence of hydrogen in the nitrogen. By combining the use of bauxite with the introduction of hydrogen into the gas, a more than cumulative effect results. In this way the reaction can be rendered practicable at 1,500° C. or so.

CHAPTER V.

SURFACE ACTION.

IN the present chapter it is proposed to present some account of the catalytic influence of surfaces upon chemical reactions. Now, as far as practical utility is concerned, the only process in which this influence has been at all investigated is that of combustion. A few observations relating to the *rôle* played by the walls of the containing vessel are to be found in chemical literature, but these are hardly worthy of notice here. Cold surfaces, of course, are ruled out of consideration, for their influence is well known to be the antithesis of catalytic; indeed, it is to the retarding effect of cold surfaces upon fuel combustion that we owe the present smoke and soot nuisance. The discussion, therefore, narrows itself down to a consideration of the influence of hot surfaces.

The subject, in its theoretical aspect, is by no means a new one. Every student of chemistry is acquainted with Davy's discovery (1817) that a warm platinum wire, held in a non-explosive mixture of coal gas and air, continues to glow until nearly all of the oxygen has disappeared. In 1823 the phenomenon was investigated by Dulong and Thénard, and independently by Döbereiner, who showed that all solids, and not merely the members of the platinum group, as Davy thought, possess the power of promoting combustion at temperatures below the ignition point, the influence varying with the specific character and fineness of division of the solid concerned. Henry and Graham have also recorded observations bearing upon the same

subject ; whilst attempts to explain the phenomenon led, in 1834, to a long controversy between Faraday and de la Rive, of which more will be mentioned later.

With the exception of the well-known Döbereiner lamp, however, the practical application of these facts lagged far behind their recognition in scientific circles—a circumstance which was due, in large measure, to the influence of Siemens, who created the impression that contact with hot surfaces retards combustion by promoting dissociation. Starting with this erroneous deduction, it came to be generally accepted that contact between combustible gases and hot surfaces should be avoided as far as possible.

Among the few who recognised the fallacy of Siemens' reasoning, mention will be made only of Bone, for it is to this investigator and his collaborators that we owe much of our knowledge of what is called "surface combustion." As a result of his researches on this subject, begun in 1902, the following facts have been definitely established :—

(1) All incandescent surfaces are capable of accelerating gaseous combustion ; and to an approximately equal degree, for the wide differences between the catalytic powers of various surfaces at low temperatures gradually diminish as the temperature rises, until at incandescence they practically disappear.

It might be noticed, in passing, that this latter conclusion is borne out by Knietsch's experiments, mentioned in Chapter II. Thus, from Fig. 1, it will be seen that at 850° C. there is little difference between the catalytic powers of platinum, pyrites cinders, or broken porcelain in sulphuric anhydride formation.

(2) The combustion takes place *heterogeneously*, that is to say, only in layers immedi-

ately in contact with the incandescent surface, and not *homogeneously*, or equally throughout the system.

(3) The catalytic process depends primarily upon condensation or absorption of one or other (and possibly both) of the reacting gases by the surface, whereby the gases are rendered " active," probably by ionisation.

(4) The incandescent surface becomes strongly negatively electrified during the combustion.

The first of these observations is utilised in the " Surface Combustion " process now to be described ; the remainder, being associated more with the theory of the subject, will be dealt with towards the end of the chapter.

SURFACE COMBUSTION.

In this process an explosive mixture of a combustible gas and air is brought into contact with a refractory solid placed in proximity to the body to be heated. The mixture should be in the proportions for complete combustion, or with air in slight excess, and must necessarily be injected on to, or forced through, the solid at a velocity greater than the speed of ignition of the mixture. On now igniting the issuing gases, the surface of the solid rapidly becomes incandescent and the mixture continues to burn there without the formation of flame, but with the development of a large amount of radiant heat.

To make clear the *modus operandi*, two forms of apparatus, corresponding to the two fundamental types, will be described. [See also CHEMICAL WORLD, 1912, I., 198.]

The first, shown diagrammatically in Fig. 5, and known as the " Diaphragm " adaptation, comprises a diaphragm A of porous refractory material, through which the gaseous combustible mixture is

forced under slight pressure from the chamber B. Soon after ignition of the gases on the exit face, the surface layer attains incandescence and, by suitably adjusting the quantity of entering gases, the incandescence can be maintained there, without any unburnt gases escaping whatsoever. This form finds special application for domestic heating, such as roasting, grilling, etc., and more especially for the concentration and evaporation of solutions, in which case the apparatus is inverted over the concentrating pan.
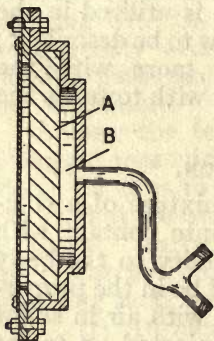
The degree of porosity is sufficient in all cases to relegate the question of back-firing beyond the need for consideration. The fineness or coarseness is determined, of course, by the quantity and pressure of the combustible mixture employed. For rich gases a fine grade is employed, whereas with poor gases and moderate temperatures a coarser grade will suffice. To avoid clogging of the pores, and the consequent necessity for the renewal of the diaphragm, the ingoing gases are preferably freed from dust. Temperatures of 800—900° C. (using coal gas) can readily be obtained by this means.

Fig. 5.—Surface Combustion Diaphragm.

In the second and more important form of the apparatus, known as the " Granular Bed," the diaphragm is replaced by a number of refractory granules, and it is then on the surface of each of the granules that incandescence occurs, rendering the whole bed a white-hot mass. Thus, in Fig. 6, is shown a muffle furnace C surrounded by lumps of refractory material D, to which the combustible

mixture in combining proportions is supplied by
the pipe E, at a velocity in excess of the speed
of inflammation of the mixture. By this means
high temperatures can readily be obtained. The
maximum naturally depends upon the working
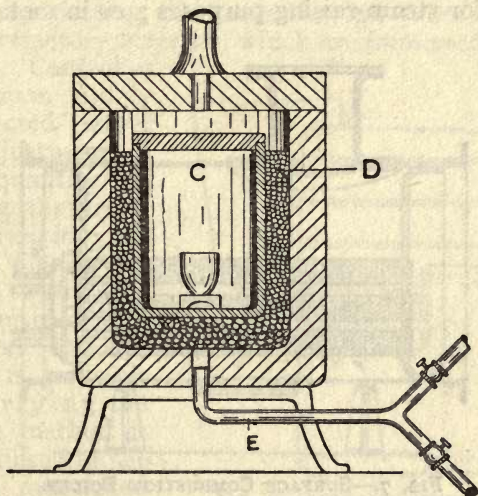conditions, but in such a furnace as just described

FIG. 6.—MUFFLE FURNACE.

temperatures in the neighbourhood of 1,400° or
1,500° C. become available.

The choice of refractory material is, of course,
determined by the temperatures involved. In the
ordinary course a number of substances are at our
disposal, e.g., calcined fireclay, ganister, etc. But
when high temperatures are in question, the number
of refractory materials is very limited. This will
be understood when it is noted that platinum can
easily be melted and even carborundum decom-
posed by this process. Practically all solids are

then eliminated, with the exception of calcined magnesia and carborundum, both, however, being subject to certain conditions.

Clearly, this second method is capable of a large number of industrial modifications. The refractory material may function as a hearth or furnace, or it may be packed into tubes which are immersed in water for steam-raising purposes ; or in metals and
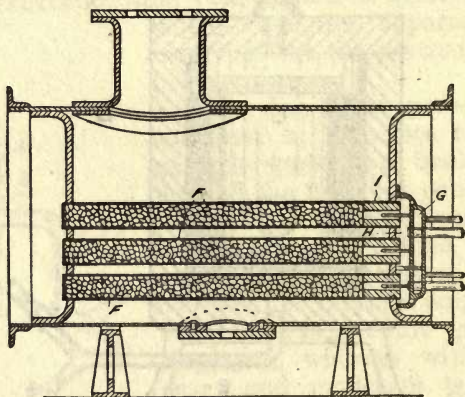

FIG. 7.—SURFACE COMBUSTION BOILER.

alloys which it is required to melt. In fact, as yet, the full range of application cannot be defined.

Undoubtedly, the generation of steam demands primary consideration. And, since in this connection three forms of apparatus are available, the description of these is considered to be sufficient for our present purpose, as covering the greater part of the field of application.

In the first form, shown in Fig. 7, the boiler is constructed on the multitubular arrangement, but each tube F is now packed with refractory granules. The constituents of the combustible

mixture are admitted to the series of tubes from feeding chambers G, H, and, being ignited, burn at or about the entrances of the tubes, which are plugged with firebrick I. The remainder of each tube serves to extract the sensible heat from the products of combustion. Any heat still remaining is employed for raising the temperature of the feed-water by passing the gases through tubes packed with refractory material, which are immersed in the water. Control of the steam supply is effected either by adjustment of the quantity of ingoing mixture or by arranging the boiler tubes in groups which can be requisitioned as required.

The principle underlying the second method is that utilised in the above-mentioned feed-water heater.

FIG. 8.—SURFACE COMBUSTION BOILER.

The fuel — in this case liquid fuel — is first burnt in a chamber J, Fig. 8, situated within, or in close proximity to, the shell of the boiler, and the resulting products are then passed through the boiler tubes K, charged, as before, with refractory material. The granular body then facilitates the heat transmission through the walls of the tube to the surrounding water by mixing the gases in transit, thereby assisting the combustion of any fuel not fully burnt originally, and by radiating heat to the walls.

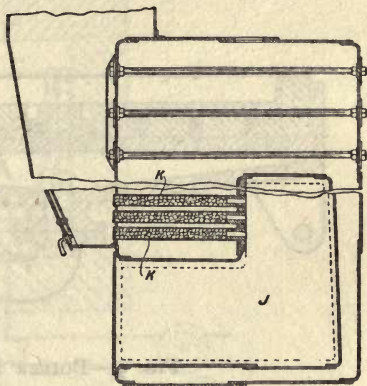The third method applies to the firing of boilers

of all kinds. Inside the flue of the boiler rails are laid down upon which run flat trays L, Fig. 9, or hearths of fireclay, firebrick or other material. The rails, preferably adjustable in height, are provided for the withdrawal of the trays ; and, to facilitate discharge of the granular material, the trays are adapted for tipping. A pipe M conveys the gaseous mixture to the hearth, uniform delivery being secured by the provision of apertures N at various points. The glowing mass developed on
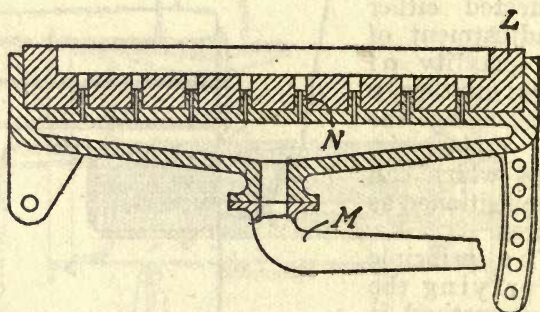

FIG. 9.—BOILER RAILS.

ignition of the mixture serves to heat the boiler in the ordinary way. Flames can be obtained, if desired, by reducing the proportion of air in the mixture and admitting a further supply to the flue to complete the combustion.

Among other applications might be mentioned, *e.g.*, the melting of metals and alloys, furnaces of all descriptions, galvanising, oil gasification and distillation, welding, etc.

The advantages of the process are manifold. In the first place, it is adapted for the employment of a large variety of combustible gases—blast-furnace gas, producer gas, water gas, coke-oven gas,

coal gas, etc., and for what have been regarded hitherto as waste gases. What is more important still, the process is remarkable for its efficiency ; in the case of tests with a gas-fired multitubular boiler, for instance, efficiencies of about 92—94% have been recorded. Moreover, the process is one of great flexibility, since the temperature can be almost instantly varied by altering the rate of feed of the
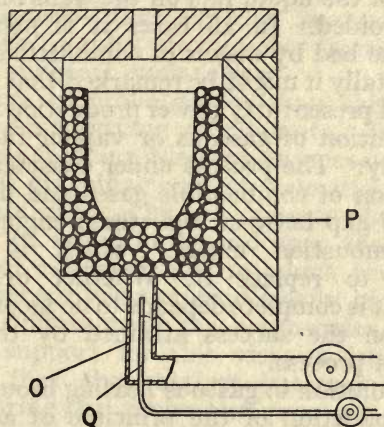
FIG. 10.—LIQUID FUEL MECHANISM.

gaseous mixture. The temperatures produced are of a high order, whilst the heat can be concentrated at any desired point.

During the last year or so experiments have been made with a view to the utilisation of liquid fuel in Surface Combustion apparatus. Already several patents have been taken out for apparatus in which the liquid fuel is first atomised by ingoing air, and the resulting mixture then delivered to the combustion bed. Such an application has already been hinted at in connection with Fig. 8. For the

purposes of illustration, the modification necessary for the furnace shown by Fig. 10 will suffice. Air under pressure passes along the outer O of two concentric tubes, and comes into contact, at a short distance from the lower face of the bed P, with a jet of liquid fuel, or of spray from an atomiser, supplied by the inner pipe Q. Seeing that the two constituents of the mixture come into contact with the incandescent bed at the time of mixing, condensation of the liquid fuel on the walls of the outer tube is avoided. In all cases it is necessary to pre-heat the bed by means of combustible gas.

Incidentally it might be remarked that the whole tendency of present-day power production is towards the substitution of gaseous or vapour fuel for the solid variety. The process under consideration, by its utilisation of combustible gases and liquid fuel, bridges the gap between the steam engine and the internal-combustion engine, which is destined ultimately to replace it. Whether or not the replacement is complete depends to no inconsiderable degree upon the success attained by the Surface Combustion process.

The revolution in gaseous heating brought about by the application of the principle of accelerated combustion by hot surfaces, which has been outlined above, is largely due to the investigations of Bone and McCourt. It is only fair, however, to record that the process and, indeed, several of the small forms of apparatus, had already been patented in the U.S.A. by Lucke ; but the British inventors are undoubtedly answerable for the extension and development of the method and the design of apparatus capable of establishment on an engineering basis.

With regard to the mechanism of the process, the fundamental fact that the surface acts as a catalyst cannot be gainsaid, nor yet the general

manner in which the surface acts. In the course of the Faraday-de la Rive controversy, already referred to, the rival theories were fiercely debated, de la Rive maintaining that surface combustion consists essentially of a series of rapidly alternating oxidations and reductions of the catalyst, whilst Faraday strongly upheld the view put forward, first by Fusinieri (1825), that the function of the solid is to condense the reacting gases upon the surface, thereby producing in the surface layer a condition comparable with that of high pressure. Bone's experiments amply prove the correctness of Faraday's physical explanation.

Attempts to probe deeper than this have not yet resulted in anything very definite. It is known, nevertheless, that incandescent surfaces emit streams of electrons travelling at high velocities ; and the action of hot surfaces in promoting combustion may ultimately be found to depend upon the formation of layers of electrified gas in which the chemical changes proceed with extraordinarily high velocity under the influence of the corpuscular discharge. Excellent support for this view is found in the discovery that the catalyst becomes negatively charged during the combustion process.

Of great interest, too, is the fact that, at temperatures below the ignition point, the activity of a surface is greatly affected by previous contact with the gases. Thus, in most cases, exposure to the combustible gas enhances the catalysing factor, whereas contact with oxygen lowers it, though to a smaller degree. After attainment of a steady condition, the rate of combustion is found to be directly proportional to the pressure, if the gases are present in their combining proportions and the products of combustion are rapidly removed. When, however, one of the reacting gases is present in excess, the rate of combustion is then propor-

tional to the partial pressure of the combustible gas.

INCANDESCENT GAS MANTLES.

From the present standpoint of surface catalysis, the subject of gas mantles possesses at least one feature of sufficient interest to render it worthy of mention.

Soon after Welsbach began his epoch-making investigations (1885) upon the luminous properties of the rare-earth oxides—the luminosity of these oxides, by the way, is not dependent upon catalysis—he came to the conclusion that, of them all, thoria appeared to be the most satisfactory as a mantle basis. But he also made the curious observation that the more the thoria was purified, the less the light obtained from it. Attempts to account for this led, in 1892, to the discovery of the power exercised by a trace of ceria in augmenting the emissivity of thoria, and to the consequent adoption for the mantle basis of a mixture of 99% thoria and 1% ceria—a mixture which numerous later attempts have failed to improve upon.

The added component is known as an " excitant." Pure thoria gives a relatively poor light, but the continuous addition of ceria gradually increases the luminosity to a maximum of tenfold when 1% is present, any further addition then diminishing the luminosity until, with 10%, the difference in effect is inappreciable. In present-day manufacture, the cotton or ramie web is impregnated with a 25—33% aqueous solution of thorium and cerium nitrates in the proportion of 99 : 1, together with a little hardening medium, e.g., beryllium nitrate, if necessary.

The reason for the beneficial action is not definitely known, though catalysis, perhaps in conjunction with other phenomena, furnishes the

likeliest explanation. Certainly, the power which many catalysts possess of existing in two or more states of oxidation applies to cerium, and the activity of ceria may perhaps be attributed to this.

In connection with the Nernst lamp, too, a similar phenomenon is to be observed, for the pure zirconia rod, which is heated by an electric current until luminosity is reached, gives much less light than does a rod containing a little thoria, ceria or like oxide.

Furthermore, it might be mentioned that it has been proposed to employ fragments of mantle in place of palladium asbestos as the catalyst in gas analysis, for the estimation of hydrogen, carbon monoxide or methane by combustion with excess of oxygen.

CHAPTER VI.

HYDROGENATION.

UNTIL quite recently, the only methods of reduction available were those based upon the utilisation of " nascent " hydrogen liberated by the decomposition of water by sodium and of acids by metals, or, if cases of exceptional difficulty were encountered and risks could be incurred, the use of hydrogen iodide in sealed vessels was resorted to. But within the last decade or so the whole subject of reduction has been carefully studied from many aspects, with the result that several methods of great value have now been worked out in detail. These have already been employed in the laboratory for the preparation of a whole host of substances, hitherto unknown to chemists or very difficult to obtain by other means ; whilst, in several instances, the laboratory process has been promoted to the industrial stage with conspicuous success.

In the domain of Organic Chemistry—and it is here that research upon reduction has been most actively engaged—the tendency has been towards the direct employment of hydrogen, *i.e.*, towards that main branch of reduction known as hydrogenation. In this way the complications introduced by the addition of extraneous material difficult of removal are avoided, and a clean, straightforward method, capable of great regulation and adaptation, results.

The direct union, however, of most unsaturated organic compounds with gaseous hydrogen is only effected by the aid of catalysts working under various conditions, viz. :—

(1) Finely-divided metals at the ordinary temperature.

   (2) Finely-divided metals at moderate temperatures.

   (3) Metallic oxides at high temperatures and pressures.

A brief discussion of each of these methods in their general outline is desirable before turning to the most important of their industrial applications.

   With the distinct method of electrolytic reduction it is not intended to deal in the present chapter, for, though its development has for some time attained the commercial stage, its interest from the point of view of catalysis is small. Reference is made to it, however, in a later chapter.

CATALYTIC METHODS OF HYDROGENATION.

   I. *Use of Finely-divided Metals at Ordinary Temperatures.*—Since the beginning of the nineteenth century it has been known that finely-divided platinum and palladium possess the property of occluding gases, particularly hydrogen, upon their surface. In the case of palladium, indeed, the effect is so marked that until recent years it was thought that one or more compounds was produced by union with the hydrogen. In any case, instances are to be found in chemical literature in which this property has been taken advantage of for reduction purposes.

   Within the last few years a revival of the method has taken place, initiated chiefly by Paal (1902), who has proposed to utilise the still further increased area which obtains in a colloid. Colloidal solutions of platinum, palladium, osmium and iridium—of which the palladium hydrosol appears to possess the greatest value—have been made by the action of some reducing agent, such as sodium protalbinate or lysalbinate, and later hydrazine, upon a solution of a salt of the respective metal. By merely passing at the ordinary temperature a current of hydrogen

through a solution of, say, nitrobenzene, to which a little palladium hydrosol has been added, aniline can be obtained in large yield. The readiness with which hydrogenation takes place has suggested the application of the method to the estimation of hydrogen in gaseous mixtures in which the proportion of this constituent is not too small. Instead of the usual mixture with oxygen and subsequent explosion, the hydrogen is absorbed by a mixture of palladium hydrosol and some unsaturated compound, e.g., sodium picrate, contained in a modified form of Hempel pipette.

A recent application of the method is to be found in the reduction of various oils, hard, brittle products being the result. The reduction of the glycerides of unsaturated fatty acids, and even of the acids themselves, has been brought about by this method—a result of no slight importance, as will be seen when the hydrogenation of oils is discussed. In these reactions, however, the palladium hydrosol is converted into the inactive gel form by the procedure necessary for the isolation of the products, and this has rendered the process a costly one on account of the high price of colloidal palladium. Now, the finely divided metal is precipitated upon inert substances devoid of anti-catalytic action, e.g., powdered nickel, magnesium, chalk or kieselguhr, and the above difficulty is surmounted (Karl).

Skita, who has done much with Paal's method, finds that the hydrogen addition takes place more quickly and completely, as well as permits of extended application, if the pressure of the hydrogen be somewhat increased.

The use of platinum, not necessarily colloidal, but prepared by a special method in the finely-divided state, has been actively investigated by Willstätter, who demonstrates that many reductions, performed at higher temperatures in the case of the

method next to be considered, can be easily accomplished by its aid at the ordinary temperature, though naturally at much slower rates than obtain in the other method. Zelinsky uses specially prepared palladium in a similar way.

The utility of the method, then, lies in its application to the reduction of compounds which are not sufficiently volatile, or are too easily decomposable, to be subjected to either of the two following more rapid methods. Examples of the results obtained by this process cannot be given here, for, with few exceptions, most of the hydrogenations can be effected by the important method now to be considered.

II. *Use of Finely-divided Metals at Moderate Temperatures.*—Moissan first observed that acetylene, when brought into contact with recently-reduced nickel, cobalt or iron, as well as platinum black, was decomposed with incandescence, carbon being deposited, a gas believed to be hydrogen disengaged, and liquid hydrocarbons, particularly benzene, produced. His explanation lay in a simple physical condensation of the gas in the pores of the metal, which was considered conducive to combination. But Sabatier, who had been investigating the fixation of nitrogen peroxide by several oxide-reduced metals, and had observed the formation of true compounds, which he called metallic "nitroxyls," thought that Moissan's explanation was untrue to facts, and that, instead, some temporary unstable compound was the intermediate product. Sabatier took up this seemingly unimportant point, and tried the effect of bringing a mixture of hydrogen and acetylene into contact with reduced nickel. Complete transformation into ethane was the result (1899), and the foundation was laid for a hydrogenation method of tremendous significance.

The principle of the method is a simple one. The vapour of the substance to be reduced is mixed with hydrogen and passed directly over specific metallic catalysts maintained at temperatures usually situated between 150° and 200° C. Such a process differs from the others already mentioned in this chapter in its extreme rapidity, since complete hydrogenation occurs during the short time the mixture is passing over the catalyst. Rapidity, however, is not the only advantage, for Sabatier and his collaborators, Senderens, Mailhe and others, who have worked on this method for some fifteen years, find it to be one which, whilst requiring the minimum of attention, furnishes very high yields.

The metals which are suitable as catalysts are nickel, cobalt, platinum, iron and copper, of which nickel is far and away the most active, while the others are arranged in diminishing activity. As would be anticipated, the practicability of the method depends largely upon the condition in which the metal is used. It must be prepared by reduction of the oxide and preferably in the same vessel in which the subsequent reduction is to take place. The activity depends both upon the nature of the oxide employed and the temperature at which it is reduced. Obviously, the greater the surface exposed the greater the activity, so that the conditions must be carefully arranged to satisfy this requirement. Reduction at a low temperature is found to yield a metal which is too active and too sensitive to external influences, while reduction at a high temperature almost reduces the catalytic power to zero. Consequently a suitable intermediate temperature must be chosen. Sabatier finds that the best nickel for the purpose is produced by dissolving the metal in nitric acid, calcining the nitrate at a dull red heat and then reducing the oxide slowly at a temperature of about 300°—325°, until water is no

longer evolved. After the nickel has been prepared as described, it is necessary to keep it out of contact with the air, as it is extremely pyrophoric and quickly loses its activity on exposure.

Weight for weight, the efficiency of pure nickel is not so great as that which has had its active surface increased by the aid of some suitable carrier. Hence many proposals have been made for combining the catalyst with a great variety of supporting bodies, ranging from pumice and kieselguhr to charcoal and sawdust.

There are two conditions for the conductance of the process, the rigorous observance of which is indispensable to success. In the first place, the materials used, whether hydrogen, metal or organic compound, must be as pure as can be obtained, for any impurity is readily absorbed by the catalyst to the detriment of its activity. Sulphur and its volatile compounds, as well as the halogens, are particularly to be avoided in this respect, and, to a lesser degree, arsenic and phosphorus with their volatile compounds. Electrolytic hydrogen, or hydrogen of equivalent purity, appears to be essential. Even then the catalyst must, sooner or later, succumb to the toxic effects of minute impurities impossible to remove, and, in consequence, the desirability of frequent renewal needs emphasis.

Again, it must be clearly recognised that a particular hydrogenation will only take place within predetermined limits of temperature, since any excursion outside of these limits will necessarily contaminate the final result with undesired subsidiary products and diminish the yield. The more difficult the reduction, the narrower is the range of temperature, and *vice versâ*. The reduction of ethylene bonds, for instance, being easily effected, is possible within a comparatively wide temperature

interval, whereas aromatic rings in general necessitate careful temperature adjustment.

In its elementary aspect the apparatus employed is shown in Fig. 11. The industrial modifications, of course, vary with the nature of the process for which they are required, but the principle of the arrangement will be evident from a consideration of the laboratory apparatus shown. The tube, B, containing the reduced metal is heated in a furnace or oil-bath, or preferably by an electrical resistance apparatus, the latter being employed where

FIG. 11.
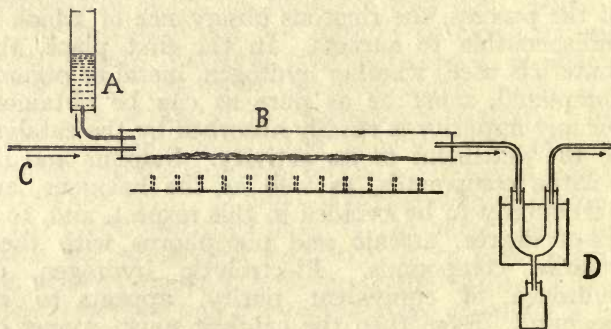
uniformity of temperature is essential. Pure hydrogen is introduced at C, and sweeps in some of the organic compound, conveniently represented as being liquid and passing in from A. If the compound is solid it is melted in a distilling bulb and the hydrogen bubbled through. Contact with the reduced metal, usually nickel, effects the reduction and the products are condensed in D.

Having thus briefly outlined the method and the conditions necessary for its success, attention will now be directed to some of the very important results obtained by its aid. A cursory glance only

can be attempted, for it must be remembered that, whereas only a few examples can be instanced, they are really legion.

Thus fatty and aromatic nitro-bodies are found to yield the corresponding amine. A practical application of this is to be found in the manufacture of aniline, for by this method, not yet fully appreciated by manufacturers, the reduction of nitrobenzene can be easily realised in a continuous way. Copper, however, is preferable to nickel as the catalyst, because it never brings about the further hydrogenation of the aniline produced. Moreover, as copper is not so sensitive as nickel to disturbing factors, water-gas or even purified coal-gas may be substituted for pure hydrogen. It might be mentioned in this connection that in the ordinary process for the manufacture of aniline by the reduction of nitrobenzene, using iron and hydrochloric or acetic acids, the iron functions in the manner of a catalyst, for only 5 % of the acid theoretically necessary is really employed.

Again, ketones of both series are readily hydrogenated. Acetone, for instance, is converted into isopropyl alcohol with an efficiency which compares very favourably with that which results from the use of sodium amalgam and, in consequence, the cost has been greatly reduced.

An interesting case is that of the monoxide and dioxide of carbon. From the former, formaldehyde, and then the commercially important methyl alcohol might be expected, whereas in both cases only methane is produced. Nevertheless, this reaction has been utilised to great advantage in a process which aims at increasing the calorific value of water-gas by eliminating the carbon monoxide constituent by passage over reduced nickel at 350°—400° C. In this way the residual coke of gasworks may be utilised for the manufacture of lighting gas.

The above reactions involve the substitution of hydrogen for oxygen in the compound. An equally important class of substances, however, fix their hydrogen by addition. This class naturally comprises most of the unsaturated compounds—double and triple link—of both the fatty and aromatic series.

In the case of simple fatty substances the addition of hydrogen is readily effected, the triple bond more so than the double, and copper is quite sufficient as the catalyst. More difficult, but of the greatest industrial utility, is the hydrogenation of unsaturated oils, which subject will be dealt with towards the end of the chapter.

The application of the method to compounds containing the aromatic nucleus is extremely wide, and includes, moreover, some of the most important reactions it is able to accomplish. Carefully reduced nickel is essential here, together with delicate regulation of the temperature. Under these circumstances such classes of compounds as the hydrocarbons, the phenols, the aromatic amines and acids can be hydrogenised to the corresponding compounds of the cyclohexane series. In fact, the method comprises the principal one known for the preparation of compounds of this type. Thus, to take some simple examples, benzene yields cyclohexane, phenol gives cyclohexanol, and aniline a mixture of cyclohexylamine, dicyclohexylamine and cyclohexylaniline. Naphthalene takes both 4 and 10, and anthracene 4, 8, 12 or 14 atoms of hydrogen, according to the temperature employed. This illustrates one of the important developments of the method, viz., the possibility it affords, by reason of the varying activity of the available metals and the temperature limits at one's disposal, of tracing a reaction step by step—a process which adds considerably to our knowledge of the constitution of the bodies under experiment.

By this means the process has been of the greatest service in the terpene and other series by the light it has thrown upon the constitution of these bodies ; while it has similarly contributed to the elucidation of other problems of no little interest to the theory of chemistry.

Of practical importance is the preparation of numerous artificial perfumes by the aid of this reaction. Moreover, it permits of the production of cyclohexanol and p-methylcyclohexanol, easily obtained from phenol and p-cresol respectively, which are used in the manufacture of isoprene and butadiene, and seem, therefore, destined to play an important part in the synthesis of rubber—a problem which is at present occupying the attention of so many workers.

The mechanism of these remarkable catalytic reductions can be explained in several ways. It may be that the passage of the hydrogen over the finely-divided metal induces its decomposition into the atomic or " nascent " state, or that the temporary occlusion of the hydrogen upon the catalyst favours its interaction with the reducible body. A more probable explanation is that put forward by Sabatier himself, who supposes the formation of an intermediate unstable hydride upon the surface of the metallic catalyst, this hydride being capable of furnishing its hydrogen rapidly and in a suitable state to a substance which is able to utilise it. There might even be a series of hydrides formed, in which case the varying degree of activity of the different metallic catalysts would be explained, since, then, the most powerful catalyst would be capable of forming the greatest number of hydrides. Seeing that it was this idea which led him to initiate his remarkable researches and has served as guide throughout, its utility provides a strong argument in its favour. When the subject of dehydrogenation

is dealt with in the next chapter, it will be found to provide still further support to the above theory.

If only the existence of these compounds could be proved in some independent way, it would remove not a little of the uncertainty which rests upon the subject of catalysis in general.

III. *Use of Metallic Oxides at High Temperatures and Pressures.*—Nickel oxide heated to 200° in an atmosphere of hydrogen is reduced to metallic nickel, but if benzene be present it is found to be transformed into the hexahydro compound in the presence of this oxide at considerably higher temperatures without appreciable production of the metal. Observations of this nature, due to Ipatiew, led him to study the *rôle* of nickel and other oxides under the conditions of high temperatures and pressures in catalytic hydrogenation, with the result that we now associate with his name the method underlying his researches. Briefly stated, this method consists in bringing hydrogen at a pressure of at least 100 atmospheres into contact with the substance to be reduced in the presence of nickel or other suitable oxide heated to temperatures above 250°, and contained in a specially-constructed steel tube. His latest investigations have been concerned with the catalytic action of iron and copper oxides.

One circumstance which affects the course of the reaction is deserving of mention, viz., that if the oxide be heated to a high temperature before use, its efficiency as a catalyst is greatly impaired. This effect seems to be due, not so much to the production of a different surface, as to the elimination of moisture, for in the presence of the latter the reduction is stated to be facilitated. Its influence may be explained on the assumption that the water reacts with the oxide to liberate active hydrogen. As might be expected, there are many chemists who think that under the conditions of the process the

oxide is reduced to the metal, which latter really functions as the catalyst.

It is unnecessary to mention any of the many accomplishments of the method, for it possesses no advantage over the preceding method except in its application to the reduction of compounds which demand a high compression of hydrogen. Naturally its dangerousness precludes the industrial development of the method. Very recently, by satisfactory industrial tests, Bedford has asserted the superiority of oxides of nickel over the metal itself, employed, however, without high pressures of hydrogen. The oxides are stated to be much less sensitive to certain impurities, and the hydrogenation proceeds with greater velocity than with nickel itself.

HYDROGENATION OF OILS.

Liquid vegetable oils are of much lower value than solid fats, the former being in many cases produced as a by-product in the manufacture of the solid varieties, and on this account chemists have repeatedly attempted the conversion of the one into the other.

The nature of the problem will be understood when it is recalled that most liquid oils are made up of olein, the triglyceride of oleic acid, whereas solid fats are largely stearin or palmitin, the triglycerides of stearic and palmitic acids respectively. Moreover, oleic acid itself is a liquid, whilst stearic and palmitic acids are solids. A glance at the constitution of these acids reveals the important fact that, whilst oleic acid is unsaturated, the two remaining acids are saturated, oleic acid, however, otherwise corresponding to stearic. Reduction, therefore, should bring about the conversion of oleic into stearic acid, and of other unsaturated acids, such as erucic, linolic, linoleic, etc., acids into the corresponding

saturated compounds ; but, for many reasons, so simple a solution of the problem proved impracticable until Sabatier and Senderens introduced their method.

Previous processes on other lines had not met with much industrial success. The only one which proved of any value involved the treatment of oleic acid with strong sulphuric acid and subsequent separation by distillation of the resulting hydroxystearic and other solid acids (Frémy).

Soon after the publication of the researches of Sabatier and his co-workers, patents were taken out by Leprince and Siveke (1902) in Germany, and by Normann (1903) in England, for processes based upon their principle. The latter patent, it is interesting to note, already widely known by reason of its alleged fundamental character, has recently been revoked (see CHEMICAL WORLD, 1913, 2, 325). Since the time of these patents many others have appeared for modification in the working of the process, for improved machinery, etc. The work of Willstätter and of Paal in the first-named connection has already been mentioned.

It was a feature of the above patents that, whilst saturation might be effected by causing the vapours of the oil together with hydrogen to pass over the catalyst, hydrogenation results in a satisfactory manner merely by exposing the oil in the *liquid* condition to the action of hydrogen and the catalyst. The significance of this will be realised when it is remembered that glycerides cannot be vaporised without undue decomposition. As a result of this discovery, then, the working material is not usually gasified as a preliminary to hydrogenation, but is brought into contact with the catalyst as a fine spray, or the catalyst is added to the liquid and intimate contact ensured by agitation or other means. In any case, the oil is heated to a suitable

temperature, about 200—250° C., whilst purified hydrogen is injected into the catalyser. The hydrogen is usually under a pressure of a few atmospheres, but this is not indispensable. Indeed, it has been shown recently that reduction can take place even under reduced pressure (Zelinsky). For an account of the various kinds of apparatus employed, see *Journ. Soc. Chem. Ind.*, 1912, *31*, 1155.

The two essentials of the process are concerned with the production of an active catalyst and with the problem of a cheap hydrogen supply.

With regard to the former, some form of nickel is generally employed, because of its low cost and high efficiency. But recently palladium has received some attention, on account of its extreme efficiency, though its initial cost is against it ; whilst other metals, *e.g.*, platinum, copper, iron, etc., have been used to some extent.

The hydrogen necessary for the process is now available from several sources. By one method, suitable for large plants, steam is decomposed by heated iron sponge with the formation of hydrogen and ferric oxide, the iron of the latter being regenerated by reduction with water-gas. For small plants the electrolysis of water is resorted to, particularly when electric power is cheap. A very promising method provides for the removal of carbon monoxide and hydrocarbons from water-gas by liquefaction ; whilst another involves the passage of water-gas and steam at a temperature of 500° C. over lime containing an iron catalyst.

The resulting " hardened oils " are of great commercial utility. Besides being suited for soap and candle making and as lubricants, there is nowadays the possibility of their utilisation as edible fats. As to the likeliness of this latter application, it is difficult to give any definite opinion, for experts

are at present investigating the question of contamination with the finely-divided nickel employed.

The hydrogenation of oils, however, by this method is already being practised on a large scale in England and Germany, and its extensive development in the future can be confidently relied upon.

CHAPTER VII.

DEHYDROGENATION AND OXIDATION.

WE turn now to a consideration of the catalytic dehydrogenation and oxidation of organic compounds.

When dealing in the last chapter with Sabatier's method of catalytic hydrogenation, attention was drawn to his explanation of the mechanism of the process on the lines of the formation of intermediate unstable metallic hydrides. If now this conception be correct, it would be anticipated that the catalysts employed in that process would be able to unite with hydrogen existing not only in the free state but also in compounds capable of surrendering it. In other words, catalysts of hydrogenation should be catalysts of dehydrogenation too. Such is, in fact, found to be the case, and Sabatier, with his collaborators, has thoroughly explored this field of research.

Apart from the state of the catalyst, fairly high temperature is the essential condition. Since hydrogen is liberated, the reverse reaction then sets in to some extent, but the concentration is not sufficient to produce a very serious diminution in the percentage yield. The most important of the applications of the method are briefly summarised below.

(1) *Degradation of Hydrocarbons.*—All hydrocarbons, when submitted to a high temperature, are decomposed with the partial formation of lower hydrocarbons. In the presence of catalysts, however, the decomposition can be brought about at much lower temperatures and, therefore, with far

greater regulation than obtains in analogous pyrogenic decompositions.

Thus, the compounds produced by hydrogenation of stable cyclic compounds tend to revert to the original body if the temperature at which hydrogenation took place be appreciably raised. Cyclohexane, for instance, gives benzene, cyclohexanol regenerates phenol, piperidine reverts to pyridine, etc. The dehydrogenation may even be progressive, as in the case of dodecahydroanthracene, which loses its hydrogen in the reverse manner of that in which the anthracene initially took hydrogen up.

Ordinary cyclic compounds and chain hydrocarbons, in contact with divided metals at temperatures more or less elevated, also appear to split up step by step into hydrogen and a less hydrogenised hydrocarbon. The loss of hydrogen appears to be accompanied by the scission of the hydrocarbon molecule into CH_3, CH_2 and CH groups, which then rearrange themselves into a further complex molecule whose empirical formula is poorer in hydrogen than that of the original hydrocarbon.

Only by the postulation of such an hypothesis can the curious results obtained by passing various hydrocarbons over heated nickel be explained. If acetylene, for example, be treated under these conditions at 250—300° C., carbon and hydrogen are produced, together with certain hydrocarbons. These latter, if hydrogenated at 180° C., yield a liquid closely resembling Baku petroleum ; whereas, if the temperature be raised to 300° C., Galician petroleum is the product. From acetylene and hydrogen at 250° C. or so, the condensed product resembles the petroleum of Pennsylvania, being a fluorescent mixture of the typical hydrocarbons.

The whole reaction is a combination of hydrogenation, dehydrogenation, decomposition and polymerisation. Anyhow, it has thrown considerable

light upon the *raison d'être* of the petroleum found in the earth's crust. For while some authorities consider this to be formed by the action of water on metallic carbides or by the destructive distillation of animal matter far beneath the surface, Sabatier argues that strata of reduced metal, at the temperatures which characterise the upper portions of the earth's crust, play the predominant part by promoting such a reaction as the above between the simpler hydrocarbons and hydrogen which result from the interaction of water and carbonaceous matter at the high temperatures prevailing in deeper regions.

While dealing with this subject, attention should be turned to a very recent process for the conversion of petroleum into petrol. In this process, a continuous feed of petroleum and of hydrogen under pressure are passed from the bottom into a still containing nickel as the catalyst, which is heated to a degree sufficient to vaporise the resulting petrol. The latter is carried away by the hydrogen to the condenser, while the heavier hydrocarbons produced drop back into the still. The explanation of the reaction is as follows : Petroleum, a saturated compound, is decomposed and dehydrogenised with the production of a saturated compound such as petrol, and a heavier unsaturated compound, which immediately takes up hydrogen to form a saturated body, and this again splits up into petrol and an unsaturated compound. And so the cycle is repeated indefinitely until the nickel becomes inactive and the petroleum in the still is overloaded with tarry matters.

In the degradation of hydrocarbons generally, finely-divided and recently-reduced nickel displays the greatest activity. Cobalt is somewhat less active ; iron begins to behave as a catalyst above 350° C., and platinum, as well as copper, above about 400° C.

(2) *Dehydrogenation of Alcohols.*—Long ago it was observed by Berthelot that the vapours of alcohol when passed through a hot tube suffer decomposition at 500° C. into ethylene and aldehyde. That is to say, under the influence of heat, both dehydratation, or loss of water, occurs, and dehydrogenation, or loss of hydrogen. Subsequent experiments have shown that all primary alcohols decompose in this way when subjected to a temperature of about red heat. The simultaneous dehydratation, and dehydrogenation may be represented thus :—

$$C_n H_{2n+1} . CH_2 . CH_2OH \longrightarrow \begin{cases} C_n H_{2n+1} . CH = CH_2 + H_2O \\ C_n H_{2n+1} . CH_2 . CHO + H_2 \end{cases}$$
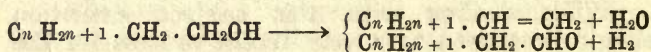
Secondary alcohols under similar conditions revert even more readily into unsaturated hydrocarbons and ketones.

By the aid of catalysts, now, the decomposition can be realised at much lower temperatures. And, what is of greater importance, one or other of the two reactions can be made to predominate according to the nature of the catalyst selected.

Finely-divided metals, such as copper, cobalt, nickel, iron, platinum, and palladium, catalyse almost exclusively the dehydrogenation process. The same applies to a small number of anhydrous oxides, chief among which are the lower oxides of manganese, tin, uranium, molybdenum, vanadium and cadmium, though the activity of these is less than that of the metals.

Other metalic oxides, on the contrary, such as thoria and alumina, are catalysts only of dehydratation; whilst there exists, too, a large number of substances which can function to a varying degree as catalysts for both reactions. With the question of dehydratation, however, we are not concerned in the present chapter.

The dehydrogenation of alcohols, both primary and secondary, is most readily effected by reduced copper. If a fatty alcohol be passed over this catalyst at 200—300° C., a yield of at least 50 % aldehyde or ketone can usually be condensed. Of the remainder, a very small percentage consists of superior products, whilst the larger proportion consists of the original alcohol, produced by the action of the disengaged hydrogen upon the product of the reaction in the presence of copper at about 200° C. As pointed out before, however, the conditions are favourable to splitting, because of the smallness of the hydrogen pressure. By working under reduced pressure, the inverse reaction can be diminished and at the same time the volatilisation of the alcohol rendered easier.

Cyclic alcohols may be dehydrogenised in a similar way. Borneol, for instance, can be transformed into camphor by passage over reduced copper at 300° F., whilst geraniol under similar conditions gives citral. The former fact is utilised industrially in the treatment of certain camphors which are sold very cheaply on account of their large content of borneol. As the usual process for removing borneol by means of nitric acid is very slow and unsatisfactory, the above dehydrogenation method, which yields nearly pure camphor, has found ready application in this field.

Of the other catalysts, cobalt, iron, platinum, as well as the above-mentioned oxides, are less advantageous. Zinc is stated to possess high activity. Nickel is ruled out on account of the violence of its action, for it pushes decomposition too far.

The general design of the apparatus employed by Sabatier and Senderens, to whom we owe most of our knowledge of this subject, is the same as that shown in Fig. 11, except, of course, that the leading-in tube for hydrogen is suppressed.

We come now to the most important of the industrial applications of this reaction, viz., the preparation of formaldehyde from methyl alcohol. At the outset, it may be remarked that the classification of the process as a dehydrogenation instead of an oxidation process is, as will be seen later, in accordance with recent established opinion upon the theory of the subject.

The earliest recorded production of formaldehyde is to be found in the classic experiment of Hofmann's (1867), in which a red-hot coil of platinum wire suspended over methyl alcohol in a beaker continues to glow there so long as it is in contact with a mixture of the vapour and air.

This method forms the basis of most of the subsequent attempts and of the present commercial process. Thus, in Trillat's method (1889), which was the first proposed for large scale production, crude methyl alcohol was evaporated and passed, together with air aspirated in, through a heated vessel containing platinised asbestos. The containing vessel was heated to dull or red heat according to the nature of the catalyst, which might be copper oxide, porcelain, firebrick, coke, etc., instead of platinised asbestos.

Copper gauze, moreover, had previously been proposed by Tollens and Loew, and in modern plants this is the usual contact substance, though sometimes it is silver-coated. Occasionally silver itself is employed, whilst recently gold has been stated to possess the greatest activity. These metals, of course, are distributed over an earthenware surface. The alcohol is not now evaporated and mixed with air, as in Trillat's method, but air is driven through wood spirit kept at a temperature suitable for saturation and the mixture then passed into the catalyser. For this purpose, scrubber and carburettor arrangements have been proposed.

An innovation, due to Orloff, is of interest from our point of view. In order to start the oxidiser without the application of external heat, small pellets of platinised asbestos or pumice, known as "ignition pills," are arranged so that the gases come into contact with them before reaching the catalyst proper.

Although the bulk of the world's production of formaldehyde is obtained from methyl alcohol, various proposals have been brought forward for the employment of other initial materials. The oxidation of methane, for instance, has been suggested by Glock (1898). The hydrocarbon, or gases containing it, is mixed with an equal quantity of air and passed through a tube containing granulated copper, pumice or asbestos heated to 600° C. After cooling, the remaining uncondensed products are again passed through a second tube of contact substance, and this is repeated until all the methane is oxidised.

Theory originally considered the production of formaldehyde from methyl alcohol as essentially a process of oxidation, with a secondary oxidation to formic acid, carbon dioxide, carbon monoxide and water. No evidence of formic acid, however, can be found, but always a trace of hydrogen. These facts are in accordance with the established explanation, put forward by Le Blanc in 1911, that the main reaction is one of dehydrogenation, on the lines of Sabatier's catalytic decomposition of alcohols generally into aldehydes or ketones.

Wieland has recently attempted to show (1913) that many apparently true oxidation processes are really processes of dehydrogenation. The oxidation of an aldehyde, for example, may be regarded in this light, for in the form of their hydrates, aldehydes are deprived of hydrogen to give acids.

$$R-C\overset{\displaystyle OH}{\underset{\displaystyle H}{\langle} OH} \longrightarrow R-C\overset{\displaystyle OH}{\underset{\displaystyle O}{\langle}} + H_2$$
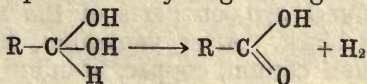
Indeed, oxidation and reduction may both be regarded as results of the same process, viz., dehydrogenation.

Furthermore, in so many cases, a catalyst deprives a substance of its hydrogen, losing its activity in so doing, and the activity is only restored by treatment with oxygen or in the presence of another hydrogen acceptor or reducible body. This explains why such substances as palladium, copper, etc., act as catalysts both of oxidation and reduction processes.

OXIDATION.

The most important processes involving catalytic oxidation are inorganic in character, and most of these have already been dealt with in Chapters II., III., and IV. Scattered throughout the domain of organic chemistry, however, are a multitude of catalytic reactions which can be classified under the general heading of oxidation processes. It is intended to devote most of the remainder of this chapter to a brief survey of these processes. Oxidation by electrolysis and fermentation will be dealt with in a later chapter.

(a) *Colour Industry.*—One of the most valuable dyes in the whole range of synthetic colours is aniline black. This dye is prepared by the oxidation of an acid aniline salt with manganese dioxide, lead peroxide, chromates, ferric salts, permanganates and chlorates, in the presence of certain metallic salts which act as carriers and are essential to the production of the black. The most remarkable of these carriers is vanadium pentoxide. According to Witz (1876), the addition of one part of the oxide to the mixture of aniline salt and chlorate is sufficient to convert 270,000 parts of the aniline salt into aniline black. After vanadium, in order of efficiency come cerium, copper, uranium and iron,

employed in the form of various salts. Recently it has been claimed that osmium tetroxide possesses superior activity. All of these metals, it will be noticed, are capable of two degrees of oxidation.

In 1907, Green patented a process for the production of aniline black in which the oxidation is effected by the atmospheric oxygen, instead of by the use of an oxidising agent, thereby avoiding " tentering " or weakening of the fibre on which the dye is developed. The process depends upon the discovery that the addition of a small quantity of a paradiamine or a para-amidophenol to a mixture containing aniline and an oxygen carrier, such as a copper salt, greatly accelerates the atmospheric oxidation. The reaction is believed to be effected by the joint catalytic agency of the metallic carrier, associated with an organic body of the type above mentioned.

Fuchsine or magenta is another important dye whose preparation involves the use of a catalytic agent. Formerly arsenic acid was used for the oxidation of " aniline oil for red "—a mixture of about one part aniline with two parts o and p toluidines—but it has now been replaced by nitrobenzene or formaldehyde. In the case of nitrobenzene, metallic iron or ferrous chloride is added to the mixture and serves as an oxygen carrier. Ammonium vanadate may also be used.

In the production of methyl violet from dimethylaniline using chlorate as the oxidising medium, cupric chloride is always added on account of its catalytic properties. When chlorate is dispensed with and atmospheric air employed, the phenol which is then added is supposed by some to act as a catalyst too.

The synthesis of indigo by Heumann's process (1890), which is worked by the Badische Anilin u. Soda Fabrik, incorporates a splendid example of

the catalytic acceleration of a reaction. The starting point of the synthesis is the oxidation of naphthalene into phthalic acid, and it was the accidental discovery of the catalytic influence of mercury when strong sulphuric acid is employed—the result in fact of the breakage of a thermometer in one of the experimental tanks—which has rendered practicable the commercialisation of this elaborate synthesis.

As it happens, mercuric sulphate is much the most powerful catalyst of the process of oxidation by means of sulphuric acid. The sulphates of potassium, magnesium, etc., are inefficacious, whilst those of iron and nickel act but feebly. Only copper sulphate can replace mercuric sulphate, and then without advantage. A mixture of the two sulphates of copper and mercury, nevertheless, displays an activity greater than the sum of both taken separately.

Incidentally it might be mentioned that mercury possesses a parallel catalytic effect in the Kjeldahl process for the estimation of nitrogen in an organic body.

Though not oxidation processes, there are several catalytic reactions in connection with the colour industry which are conveniently dealt with at this stage. These reactions are concerned chiefly with the application of hydrosulphite-formaldehyde compounds to the discharging of colours.

In 1905, Baumann and Thesmar observed that the power of these bodies to destroy the colour of a whole series of dyes, such as naphthylamine claret, chloranisidine orange, benzidine brown, etc., was greatly facilitated by the addition of an alkaline solution of an iron salt. Salts of nickel and tin were also found to have a beneficial effect, whereas almost all other metallic salts had no influence whatever.

A year later it was discovered by Wilhelm that minute quantities of certain dyestuffs themselves increased the discharging effect—an observation quite as surprising as that of the effect of vanadium salts upon the production of aniline black. Thus, the Badische firm have shown that a very small quantity of induline scarlet present in the discharge paste greatly facilitates the destruction of the colour of many dyes. Setopaline and patent brown act in a similar fashion.

The above means for increasing the reducing power of hydrosulphite-formaldehyde compounds upon azo colours has also been found applicable to the discharge of indigo, thioindigo and similar dye-stuffs, a reaction which had previously presented great difficulty. One part of anthraquinone or induline scarlet to 1,000 of the discharge paste is quite sufficient to give the required effect.

(b) *Preparation of Organic Acids.*—The laboratory method for the preparation of oxalic acid consists of the oxidation of sugar or starch by means of hot nitric acid. This method was formerly employed upon a large scale, but has since been superseded by other processes. It is possible, however, that the method may be revived, as a result of the discovery by Naumann (1905) that the addition of a trace of vanadic oxide—1 gm. per 1,000 gms. of sugar—greatly accelerates the reaction. Using this catalyst, the reaction proceeds at the ordinary temperature, and higher yields are obtained owing to the suppression of intermediate products such as saccharic, mucic and tartaric acids.

In a recent German patent, the presence of molybdenum compounds is stated to accelerate all reactions, including the above, in which nitric acid is used as an oxidising agent.

Acetic acid, again, is another acid which can be

prepared catalytically. Alcohol, placed in a vessel over which spongy platinum is arranged with free access to the air, undergoes slow oxidation to acetic acid. The product is a very pure one, but the process is not practised on an industrial scale on account of the high initial cost of the platinum. The catalyst suffers practically no deterioration.

(c) *Purification of Illuminating Gas, etc.*—The removal of the injurious sulphuretted hydrogen from lighting gas is invariably effected by passing the gas through moistened absorbent materials, chief among which are lime, ferric oxide, and manganese dioxide.

The latter two materials may be regarded as functioning in a catalytic manner, for when they cease to absorb, exposure to the air reconverts them into the original material. In the case of ferric oxide, the absorption manifests itself by a change in colour from black through reddish-brown to a dirty green, the change being due to the gradual production of sulphide. Revivification results in the deposition of the sulphur and reproduction of the oxide. The changes are usually represented :—

$$\begin{cases} Fe_2O_3 \cdot H_2O + 3H_2S = Fe_2S_3 + 4H_2O \\ Fe_2O_3 \cdot H_2O + 3H_2S = 2FeS + S + 4H_2O \end{cases}$$
$$\begin{cases} 2Fe_2S_3 + 3O_2 = 2Fe_2O_3 + 3S_2 \\ 4FeS + 3O_2 = 2Fe_2O_3 + 2S_2 \end{cases}$$
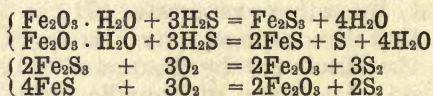
Artificial iron oxide is generally found to be more vigorous than the natural bog iron ore. Manganese dioxide, in the form of Weldon mud, is now replacing ferric oxide, for it, too, can be readily revivified and possesses besides an affinity for sulphuretted hydrogen which is from four to five times as great as that of bog ore. Lime, when spent, is thrown away and does not therefore act as a catalyst.

The catalytic function of ferric oxide and manganese dioxide is emphasised by a modern development in gas purification, in which the spent oxide

is revivified *in situ*. This is effected by admitting a certain amount of air with the gas and has the advantage of enabling the purifiers to be worked much longer without recharging.

Ferric oxide or Weldon mud also acts as a carrier for the active oxygen of saltpetre or other oxidiser used to purify caustic soda of sulphides and thio-sulphates.

(*d*) *Paint Industry.*—The drying of the oil which forms the most important constituent of paints, varnishes, etc., is such a slow process that it is usual to add to the oil some material, known as a " siccative," which accelerates the " drying " or hardening. These bodies furnish a good example of a particular type of catalysis mentioned in Chapter I.

First, it should be noticed that the drying process *per se* is a catalytic one. Broadly speaking, hardening is the result of the absorption of oxygen from the air whereby intermediate products—usually considered to be peroxides—are formed which catalyse the formation of still more of the products, the latter being ultimately changed into some indefinite compound. In the case of linseed oil, the final product is " linoxyn." The main reaction is, therefore, one of auto-catalysis.

That this is the case will be seen from Fig. 12, which represents the alteration in weight of a drying oil upon exposure to the air in thin films. The very shape of the curve, S-shaped, is typical of an auto-catalytic process.

OA represents the " induction period " during which the weight of the oil remains fairly constant, whilst small quantities of peroxides, the natural driers, are being produced. At A, the accumulation of peroxide is sufficient to effect a notable increase in the absorption of oxygen, and from that point the reaction proceeds with gradually increasing

rapidity until, at B, a maximum is reached. Beyond that point slackening occurs, consequent upon the decreasing concentration of the reacting substances.

When a siccative is employed the induction period is reduced, but the S-shape of the curve is still maintained (see curve OCB). The siccative, therefore, functions as a pseudo-catalyst, since it accelerates the production of the auto-catalyst.

As might be anticipated, the most powerful driers are themselves comparatively unstable peroxides. Manganese dioxide and red lead are those most commonly employed, though many other
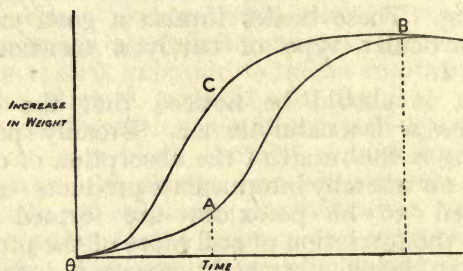
FIG. 12.

metallic oxides possess some degree of activity. Recently, Fokin has shown that cobalt compounds possess greater activity than those of either manganese or lead. Such organic substances, too, as turpentine, which absorb oxygen with the probable formation of peroxides, possess some capacity for acting as driers. Rosin is another body of this class, and combined with manganese or lead produces a good drier. The same applies to manganese linoleate, lead oleate and the like, which, being soluble in both turpentine and linseed oil, are known as " liquid driers." Whatever drier be employed, the quantity necessary is very small.

In the case of manganese dioxide, for instance, 5 lbs. per ton of oil is all that is required.

In the manufacture of linoleum, numerous attempts have been made to accelerate the slow hardening process, but in all cases the resulting product has been inferior to that obtained from the unassisted oxidation of the linseed oil.

CHAPTER VIII.

DEHYDRATION, HYDROLYSIS, ETC.

In the detailed study of Organic Chemistry, many compounds are encountered which can be prepared either from another body by loss of the elements of water or by means of a reaction in which the elimination of water is the characteristic feature. So far as Industrial Chemistry is concerned, however, most of the products obtained by this general process of dehydration, as it may conveniently be called, result from reactions in which an alcohol or an acid is the primary reagent.

With alcohols, loss of water can occur in two ways—either with the formation of an ether or of an unsaturated hydrocarbon. Or the alcohol can be made to react with acids, or with ammonia, sulphuretted hydrogen, etc., to produce a compound whose constitutional formula differs from the sum of those of the reacting bodies by the elements of water.

Acids in a similar way may be made to yield ketones by simple dehydration, or to produce aldehydes by a reaction with formic acid in which water is eliminated.

Each of these main reactions will be considered in turn.

(a) *Production of Ethylene Hydrocarbons.*—Ordinary alcohol, heated to 160—170° C. in the presence of concentrated sulphuric acid or preferably syrupy phosphoric acid, is dehydrated with the evolution of ethylene. The acid in this case, however, plays the

part rather of a desiccating agent than a catalyst, and the same applies to zinc chloride in this and other connections.

As true catalysts of dehydration, Sabatier—whose work on the catalysing power of oxides has already been mentioned—has shown that there are none to compare with thoria, alumina, titanium dioxide, and the blue oxide of tungsten. Thus, if a fatty alcohol be passed over thoria heated to 350—400° C. in an apparatus such as that shown in Fig. 11, decomposition takes place with the formation of an ethylenic hydrocarbon which can be condensed or collected in the gaseous state.

The efficiency of the catalyst is naturally greatly dependent upon its physical state ; precipitation and desiccation at a low temperature are essential. In the case of alumina, for instance, ignition must not be so intense as to destroy the solubility of the product in acid or alkali. Thoria has the advantage over alumina that it is less liable to contamination and can be purified by ignition to redness without loss of activity.

Sabatier explains the above reaction in his usual way on the basis of the temporary formation of an unstable compound, in this case a " thorinate." The production and subsequent decomposition of the " thorinate " may be represented as follows :—

$$ThO_2 + 2Cn\ H_{2n+1} = OH = ThO\ (OCn\ H_{2n+1})_2 + H_2O$$
$$ThO\ (OCn\ H_{2n+1})_2 = ThO_2 + H_2O + 2CnH_{2n}.$$
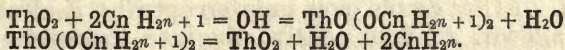
The equations represent the course of the reaction above 300° C.; below 300° C., an ether may be produced, as will be seen later.

Furthermore, Sabatier has demonstrated that the small quantity of sand usually introduced into the vessel in which ethylene is being produced by the action of sulphuric acid upon alcohol to prevent bumping, also acts catalytically. Anhydrous alumi-

nium sulphate proves to be a much more powerful catalyst, both for hydrocarbon and ether production. With the higher alcohols, the chief product is an olefinic hydrocarbon. Clay, used in the form of small balls, has been found by Bouveault to possess quite surprising activity.

Though not a dehydration process, it is worthy of observation that olefines may also be obtained by passing the vapour of a paraffin monohalide over heated reduced nickel or copper, the resulting olefine and haloid acid being prevented from recombining by passage through potash. The chlorine derivatives decompose below 260° C., but the bromo and iodo compounds require higher temperatures. It is found, too, that barium chloride exerts a similar catalytic effect at 300° C., and to a lesser extent the chlorides of lead, iron, cadmium and cobalt, all of which metals, it will be noticed, may function divalently. Chlorides of monovalent metals are inactive.

(b) *Production of Ethers.*—In Williamson's (1854) well-known explanation of the formation of ethyl ether from alcohol and sulphuric acid at 140° C., the *rôle* attributed to the acid is that of catalyst. Intermediate ethyl sulphuric acid is formed, and assumed to combine with further quantities of alcohol to produce ether and regenerate the sulphuric acid. Ether distils over uninterruptedly, if alcohol be allowed to flow continually into the mixture. The acid becomes gradually diluted with water and partially destroyed by side reactions, so that slight replenishment is necessary at intervals.

According to the later process of Kraft, ethyl ether and other members of the fatty series are prepared by the action of aromatic sulphonic acids, such as benzene sulphonic acid, upon fatty alcohols at temperatures exceeding 100° C. The reaction is explained in a similar manner to the preceding.

Schröter replaces sulphuric acid by methionic acid, $CH_2(SO_3H)_2$.

The production of fatty ethers by dehydration of the corresponding alcohols is only possible in a small number of cases, mainly the lower primary alcohols. Secondary alcohols are usually, and tertiary alcohols invariably, transformed into the ethylenic hydrocarbon. Alumina and thoria may then be substituted for sulphuric acid. Taking thoria as catalyst, the general reaction has for its second stage the interaction of the above-mentioned "thorinate," the product of the first stage, with more alcohol.

$$ThO(OCnH_{2n+1})_2 + 2CnH_{2n+1}OH = ThO_2 + H_2O + 2(CnH_{2n+1})_2O$$
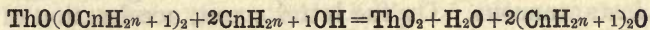
In an analogous way, it is possible to prepare the ethers of simple or mixed phenols. If phenol vapour, for instance, be passed over thoria at 390—420° C., diphenyl ether can be obtained to the extent of a 40% yield. This reaction is already practised on an industrial scale and has considerably reduced the price of diphenyl ether, which is employed in perfumery in large quantities as artificial essence of geranium. The phenol is liquefied and made to fall dropwise into the end of a heated inclined porcelain tube containing the thoria. The resulting phenol and ether are separated by a single fractional distillation and the phenol unacted upon is then further transformed. The activity of the catalyst gradually diminishes, but can be restored by calcining in the air.

The three cresols passed over thoria are decomposed in the same way giving the three cresyl ethers, the para member of which also possesses the odour of essence of geranium.

If, in the preparation of diphenyl ether, the temperature be raised over 450° C., a second reaction is introduced in which diphenylene oxide results. This, by reason of its higher boiling-point, can readily be separated from the diphenyl ether.

Mixed ethers are obtainable by the use of an aromatic and a fatty alcohol. In this way, anisol and phenetol can conveniently be prepared. The products obtained by passing the vapours of naphthol with either methyl or ethyl alcohol over thoria, comprise two perfumes which form the basis of cheap Eau de Cologne.

(c) *Preparation of Esters.*—Esters are usually prepared by the interaction of an acid and an alcohol, a process known as esterification. The reaction is analogous to the neutralisation of an acid by an alkali, but differs therefrom in being reversible and therefore incomplete, and in being far from instantaneous. On the latter count, acceleration of the process is generally resorted to by using a catalyst.

Esterification itself is an autocatalytic process, since the acid, though a diminishing quantity, can act to a certain extent as a catalyst. The process, in which an additional catalyst is employed, is differentiated therefrom by being classed as catalytic esterification.

The usual catalysts are the strong acids, hydrochloric or sulphuric acid, the latter being less efficient than the former though more generally worked with for the sake of convenience.

They are employed for the reaction when taking place in the liquid condition, but Sabatier has successfully employed some of the metallic oxides just mentioned as catalysts for esterification in the gaseous state. Thoria and alumina must be excluded, since they readily catalyse the decomposition of the acid itself, as will be seen presently. Titanium dioxide, being free from this objection, is most advantageous.

The reaction is best brought about by directing the vapours of equal quantities of the alcohol and acid (if volatile) into a column of this catalyst heated

to about 300° C. With the same velocity and at the same temperature, but in the absence of the catalyst, it is safe to say that no interaction at all would take place. When benzoic acid is one of the reacting bodies, thoria may then be employed with success. Glucinum oxide, too, heated to 300° C. furnishes a good catalyst. Charcoal and finely-divided platinum are also stated to act as catalysts, though only feebly. A small quantity of water, on the other hand, exercises a retarding effect, probably by effecting some change in the catalyst.

In the case of acid catalytic esterification, the hydrions of the catalyst are supposed to be the active agents, since the activity of different acids is in the order of their relative strengths. The activity of the metallic oxide catalysts probably depends upon their double valency.

(d) *Production of Amines and Thiols.*—Still other compounds may be catalytically prepared from alcohols by means of metallic oxides. Ammonia and the vapour of a primary alcohol, when directed over thoria at 250—350° C., furnish a mixture of a primary and a secondary amine which is easy to separate. A mixture of ammonia and the vapour of a primary amine under the same conditions yields a secondary amine. Mixed amines, of course, may be prepared in a similar way. Secondary alcohols also produce amines, but not with such readiness as in the case of primary alcohols.

Primary and secondary alcohols, together with phenols, can also be made to combine with sulphuretted hydrogen to produce good yields of thiols, if a mixture of this gas and the alcohol vapour be passed over thoria at 300—350° C.

This general method for the preparation of amines and thiols—like those for ethylene hydrocarbons, ethers and esters above—can be explained on the assumption of an unstable intermediate body.

(e) *Production of Aldehydes and Ketones.*—It remains now to consider the dehydration of acids. Certain metallic oxides, differing from those above-mentioned, are found to catalyse the decomposition of acids into aldehydes or ketones.

Symmetrical ketones result if the acid be heated to 420—450° C. in the presence of thoria, titanium dioxide, zirconia, manganous oxide, ferric oxide, cadmium oxide or even chalk. By using a mixture of acids, say benzoic acid and a fatty acid, mixed ketones are produced. In every case, the acids may be replaced by their anhydrides.

Revivification of the catalysts just mentioned can also be effected by calcination in contact with the air. Precipitated chalk, though not so effective as thoria, retains its activity even after it has become coated with carbonaceous products, but its use is only satisfactory in the case of the lower members of the fatty series and of benzoic acid. The carbonates of barium, strontium, cerium and zinc are applicable only to the preparation of acetone.

To obtain aldehydes by this reaction, a mixture of the acid with formic acid must be employed :—

$$R \cdot COOH + H \cdot COOH = H_2O + R \cdot CHO + CO_2.$$
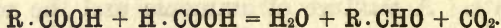
If titanium dioxide be employed at 290—300°, excellent yields are obtainable except in the case of benzoic acid. The reaction depends upon the decomposition of the formic acid with liberation of hydrogen, which then effects the reduction of the other acid.

HYDROLYSIS.

The reactions now to be considered comprise those in which the elements of water are added to a complex, followed by resolution of the product into simpler substances. The compounds capable of this treatment may be roughly classified as esters ;

amides, oximes and hydrazones ; acyl derivatives ; carbohydrates and glucosides ; and lastly, polypeptides and proteins.

In the case of most of these substances, their hydrolysis is capable of catalytic acceleration. Indeed, the hydrolysis of esters may be regarded as one of the best known instances of catalysis, for the reaction, being comparatively slow, lends itself to the study of the phenomenon. We proceed now to a more detailed consideration of the most important of these reactions. Hydrolysis by enzymes is deferred until the next chapter.

(a) *Hydrolysis of Esters.*—The simplest process, viz., hydrolysis by means of water, is an autocatalytic action, since the acid liberated functions as a catalyst. The velocity of the reaction therefore increases with the time. Naturally, the reaction is only possible in the case of the esters of comparatively strong acids. If, however, superheated steam be employed, the esters even of weak acids are affected. Thus, the hydrolysis of fats, which are natural glyceryl esters of certain fatty acids, by means of superheated steam is used as a commercial method for the production of stearic acid for candles.

Esters can also be hydrolysed by water in the presence of finely-divided metals as catalysts. At 50° C., *e.g.*, platinum black accelerates the hydrolysis of ethyl butyrate. Far better results are obtainable by the method of Sabatier and Mailhe, in which a mixture of the ester vapour with excess of steam is passed over titanium dioxide at 280—300° C. The reaction is a reversible one ; that is to say, if a mixture of fatty acid and alcohol vapour be subjected to but slightly divergent conditions, the corresponding esters are obtained, with yields rising to 70%. For acids of the benzoic acid type, thoria is of greater utility.

The usual catalysts employed, however, are acids and alkalies, both of which are used to an enormous extent in the hydrolysis—or as it is then termed, the saponification—of fats. With this branch of the subject it is proposed to deal separately at a later stage.

(b) *Hydrolysis of Carbohydrates and Glucosides.*— All di- and poly- saccharides can be hydrolysed in the presence of dilute mineral acids as catalysts, with the formation of mono-saccharides. Thus—

sucrose + water = dextrose + fructose
lactose + water = dextrose + galactose,

both of which can be expressed by the equation—

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6.$$
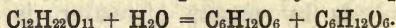
The hydrolysis of sucrose or cane sugar is another of the best known examples of catalysis, for its course can be followed by the change in optical rotatory power. It is on account of the change in sign of the optical rotatory power that the reaction is commonly referred to as the " inversion " of cane sugar. The process is of importance industrially, for invert sugar is employed as a permissible addition in the manufacture of wine. It might be noticed that in obtaining cane sugar, the presence of invert sugar may prove undesirable, so that it is necessary to take care that no inversion takes place by the carbonic or sulphurous acid used for saturation.

Starch is an example of a poly-saccharide which undergoes hydrolysis by mineral acids, in this case with the final production of dextrose (glucose)—

$$(C_6H_{10}O_6)_n + nH_2O = n(C_6H_{12}O_6).$$
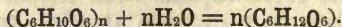
This reaction forms the basis of certain methods for the manufacture of glucose. Potato or maize starch is stirred up with water and the mixture run into boiling dilute sulphuric acid. When the hydrolysis is complete, the product is run into other tanks, the acid is then neutralised with chalk, and

the clear solution containing the glucose evaporated under reduced pressure. The use of sulphuric acid is attended by certain disadvantages, but though other acids, such as hydrochloric, oxalic and of late hydrofluoric acids, have been tried, it still remains the usual agent.

The hydrolysis of glucosides can be fairly easily effected by the use of acids, though much less readily—as will be seen in the next chapter—than when the appropriate enzyme is employed.

(c) *Hydrolysis of Proteins and Polypeptides.*— Hydrolysis of proteins by acids has been employed by E. Fischer with conspicuous success in his attempts to determine the constitution of those very complex bodies and as a means to their quantitative estimation. The use of strong acid in hot solution leads to the degradation of the protein into amino-acids, but with dilute acids or alkalies at lower temperatures, two or more amino-acids remain linked together and the result of the hydrolysis is a mixture of proteoses, peptides and peptones. Enzymes are also useful hydrolytic agents.

Conversely, acids are employed in the synthesis of amino acids and their linking up to form polypeptides.

SAPONIFICATION.

As previously mentioned, the term " saponification " is usually confined to the hydrolysis of fats by water, generally with the aid of certain catalysts. Since fats are made up of the glyceryl esters of certain fatty acids, particularly palmitic, stearic and oleic acids, it follows that the reaction results in the formation of glycerol and the liberation of these fatty acids.

It must be realised at this stage that the reaction can proceed in the absence of the saponifying agent. Superheated steam has already been described as

effective, but the temperature then becomes so high as to produce discoloration. For reasonable temperatures, the assistance of a saponifying agent must be called in, such an agent functioning in every respect as a catalyst.

The following reactions are carried out on a tremendous scale in the preparation of soaps and fatty acids.

(a) *Saponification by Bases.*—Lime may be employed in an open vat, but the amount necessary is so large—and consequently also the amount of sulphuric acid required to neutralise it—that the costliness of the process precludes its extensive employment.

The proportion of lime can be reduced by utilising the beneficial influence of pressure. If, for instance, the fat be heated with lime in an autoclave under 12 atmospheres pressure, practically complete hydrolysis is effected by the use of 1% lime, instead of the theoretical 10%. At this pressure, nevertheless, considerable discoloration of the fatty acids is developed, so that still lower pressures become necessary. In candle works, where some discoloration is of little account, the autoclaves are worked at 8 atmospheres and 3% lime for 8—10 hours. In the case of soap making, modern practice necessitates reduction to 5 or 6 atmospheres pressure.

In place of lime, magnesia and zinc oxide may be employed. Though these are not such efficient catalysts, and are besides more costly than lime, they possess the advantage of yielding no precipitate on decomposition of the autoclaved material with sulphuric acid.

Again, caustic alkalies prove efficient catalysts. In their case, an excess of the quantity required for complete neutralisation of the resulting fatty acids is employed, for the obvious reason that the resulting

salts are the constituents of soaps. There is no doubt, notwithstanding, that by the aid of pressure, complete hydrolysis could be effected by the use of only a small percentage of the quantity. The alkali—with which the fat is boiled in open vessels—acts primarily as a catalyst and only secondarily as a combining agent for the fatty acids produced. Soda with semi- or non- drying oils produces " soft " soaps ; potash with drying oils gives " hard " soaps.

Ammonia, too, has been suggested as a catalyst for the hydrolysis of oils and fats, but as its use requires the aid of pressure, no practical outcome has yet been effected.

(b) *Saponification by Acids.*—The usual acid employed is concentrated sulphuric acid. The fat, which has previously been freed from moisture by heating to 120° C. or so, is rapidly stirred for a short time in a special mixing machine with 4—6% sulphuric acid of 66° Bé. The completeness of the hydrolysis depends upon the strength of the acid ; whilst if the temperature rises at all above that found most suitable, secondary reactions, involving the production of sulphur dioxide and sulphonated compounds, are liable to occur. Indeed, for the success of the technical operation, great attention must be paid to the amount of acid, the temperature and the time of contact.

Of greater value than sulphuric acid for the promotion of this reaction is the sulpho-aromatic compound discovered by Twitchell (1900). The preparation of this catalyst is a secret, but it involves the reaction of an excess of sulphuric acid with a solution of oleic acid in some aromatic hydrocarbon, probably naphthalene. The fatty material, after having first been freed from all impurities by boiling with dilute sulphuric acid, is treated for some time with about 2% of the above reagent and half its weight of water in wooden

vessels, the mixture being heated by steam coils and kept in agitation. The emulsion is then broken down by the addition of sulphuric acid, and after standing, the upper layer of fatty acid is drawn off.

Other compounds, analogous with Twitchell's reagent, have been patented.

SUBSTITUTION.

(a) *Friedel-Craft Reaction.*—The well-known use of aluminium trichloride for bringing about the substitution of the hydrogen of the benzene nucleus by alkyl groups was first made known by Friedel and Craft in 1877. Since that time, its application has been extended to the introduction into the aromatic nucleus of other groups, *e.g.*, the preparation of aromatic ketones by the use of acid chlorides, of acids by carbonyl chloride, of aldehydes by a mixture of carbon monoxide and hydrochloric acid. Indeed, the reaction now possesses an extraordinarily varied application in organic synthesis.

In all of the above cases, the function of the aluminium trichloride appears to be catalytic. The accepted explanation of its action is based on the formation of complex intermediate compounds, some of which have actually been isolated. Anhydrous ferric chloride brings about the same kind of substitution.

(b) *Sandmeyer-Gattermann Reaction.*—The use of copper salts (Sandmeyer, 1884) or of copper itself (Gattermann, 1890) as catalysts for the replacement of the diazo group of aromatic compounds by chlorine, bromine, nitrile, nitro and thiocyanate groups is so well known as to need no further description.

It is worth noticing, nevertheless, that Erdmann has shown that when using Gattermann's method, a maximum yield can be obtained if the temperature of the copper salt solution, to which the diazonium

salt is added, is maintained at a definite optimum temperature.

(c) *Grignard Reaction.*—In the formation of an addition product of magnesium with the halide in this reaction, anhydrous ether is supposed to play the part of a catalyst. It is certainly not essential to the reaction, for the latter may take place, though less readily and smoothly, in its absence. Ether may be replaced by a tertiary amine, such as dimethylaniline.

A trace of iodine, too, accelerates the formation of the Grignard reagent.

(d) *Halogen Carriers.*—The presence of iodine or of certain metallic halides is found greatly to assist the process of halogenation. All of the metals, whose halides are efficacious, are found to be of dual valency, so that no doubt exists as to their mode of action. In chlorination, *e.g.*, the chlorides of antimony, iron, aluminium, molybdenum and thallium prove effective carriers, as well as the elements phosphorus, sulphur, tellurium and iodine. For the introduction of bromine, the above chlorides or the corresponding bromides are employed.

One of the most important technical examples of the use of a carrier is to be found in the preparation of carbon tetrachloride, destined by reason of its non-inflammability to replace petroleum spirit, ether, etc., as solvents. The method of preparation consists in the chlorination of carbon disulphide. At the ordinary temperature, chlorine and carbon disulphide react but slightly, but in the presence of iodine or antimony pentachloride, rapid formation of the tetrachloride ensues.

ISOMERISATION.

Changes in the structure of a molecule are frequently effected by the action of heat, and as

the influence of a catalyst is towards the reduction of the temperature, catalysts find application in this field.

In the industrial production of vanillin, for instance, potash is employed to transform into eugenol the isoeugenol obtained during the process. Many other transformations can be effected, such as the passage of maleic into fumaric acid by the aid of hydrochloric acid, or of aldoximes by sulphuric acid into amides, but they are of interest mainly to the theoretical chemist.

CONDENSATION.

The line of demarcation between condensation and substitution reactions, or even between these and the wider type of dehydration reaction, is very difficult to define. Under this heading, however, are usually included such reactions as involve the union of two or more dissimilar molecules with or without the elimination of component elements. In the former case, reagents are generally employed which assist the removal of these elements, but do not function catalytically. However, this is not always the case, as is shown by the Friedel-Craft reaction, which might be considered as a condensation reaction.

When no elimination takes place, the presence of a third body, acting in a catalytic manner, is usually necessary for carrying out the reaction.

Thus, the hydroxide of sodium, barium or ammonium, is employed for the condensation of o-nitrobenzaldehyde and acetone, which forms one of the steps of the indigo synthesis. Ionone, used as a substitute for essence of violets, is prepared from citral and acetone, using dilute sulphuric acid as a condensing medium. Aluminium trichloride is of service in the preparation of several vat dyestuffs,

such as violanthrone, by this process. Small quantities of benzoic or acetic acids act catalytically in the preparation of aniline blue.

Potassium cyanide is the active agent of the benzoic condensation of aromatic aldehydes. For the preparation of the leuco-base of malachite green from benzaldehyde and dimethyl aniline, acid potassium sulphate is added. Copper powder is employed in Ullmann's method of condensation, a process of technical importance in the dye industry. And so examples might be multiplied. Reference to another is found under the next heading. The above, however, are sufficient to indicate the diversity and extent of the application of catalysts in this field.

POLYMERISATION.

Engler has shown that it is possible to produce thick viscous oils by the polymerisation of amylene in the cold with aluminium trichloride—an observation which may have practical significance. Many oils, too, such as linseed oil, tung oil and castor oil, can be "polymerised" by the aid of suitable reagents, but the chemical changes undergone are not yet fully understood.

Metallic sodium has recently received industrial application as a polymerising agent in the transformation of isoprene into artificial rubber, a change which is effected merely by long contact with this agent. Other hydrocarbons are capable of polymerisation by the use of certain catalysts.

Among aldehydes, the well-known tendency to polymerisation is assisted by the presence of small quantities of bases, mineral acids and certain metallic chlorides, leading to the formation either of aldols or polyaldehydes.

As a last example, it will be sufficient to mention the formation of what are known as " phenol-formal-

dehyde "compounds. These are resinous amorphous products, which, after suitable treatment, are being utilised in rapidly increasing quantities for industrial purposes, mainly as substitutes for ebonite, celluloid, etc.

They are prepared by the condensation and subsequent polymerisation of formaldehyde and phenolic bodies in the presence of a suitable catalyst. The reaction may proceed in the absence of a catalyst, but only under such unfavourable conditions—high temperature and long contact—as render the reaction impracticable for commercial purposes. The addition of acids or acid salts greatly accelerates the process, but unfortunately their use leads to the development of undesirable by-products.

Bases, on the other hand, serve as excellent catalysts both at the condensation and polymerisation stages and enable the reaction to proceed regularly and to be kept under control. Bakelite, e.g., is obtained by the action of an alkaline condensing agent upon equal quantities of phenol and formaldehyde, the product being heated above 100° C. under a pressure of 50—100 lbs. per sq. in.

DECOMPOSITION.

The classical instances of catalytic decomposition are to be found in the influence of manganese dioxide upon the production of oxygen from heated potassium chlorate, and of finely-divided platinum upon the decomposition of hydrogen peroxide.

In the latter case, it should be remembered that any finely-divided material has a similar effect, so that the introduction of dust into the peroxide bleaching vats should be avoided. Hypochlorite solutions are decomposed in the presence of a small quantity of cobalt oxide.

The catalytic decomposition of hydrogen per-

oxide has been utilised by Ostwald in a process, known as the Catatype process, for the copying of photographs. The glass negative is rinsed with an ethereal solution of peroxide and allowed to evaporate for a definite short period. During the evaporation, the hydrogen peroxide is fully decomposed in places where the silver occurs most abundantly on the negative, *i.e.*, in the high lights, is not decomposed at all in the shadows, and but partially in the intermediate shades. The invisible positive of peroxide which has thus appeared on the photographic negative is fixed by being pressed upon a gelatine non-sensitised paper and then rendered visible by treatment with ferrous salts.

The preservative influence of certain substances has already been mentioned in Chapter I., as an instance of negative catalysis. Other examples than those given occur in the case of hydrogen peroxide solution which is preserved by a trace of acid, chloroform solution in which oxidation is prevented by a trace of alcohol, and hydrocyanic acid solution which is stabilised by traces of hydrochloric or sulphuric acids.

Conversely, a substance commonly regarded as unstable may owe its instability to the presence of some impurity whose removal would lead to beneficial results. Hypochlorite solution is a case in point. Its ready decomposition was found to be due to the presence of iron in the liquid as ferrate, and after means had been devised for the removal of this, the liquor became a regular article of commerce.

In a few cases, a substance spontaneously develops its own decomposition catalyst. Thus, the nitro-celluloses used as explosives beget acid compounds which accelerate decomposition. Counteracting substances, such as diphenylamine in this case, are added to fix the undesirable body.

SOLUTION.

The ability of certain bodies to assist the solution of others is a matter of everyday application in Practical Chemistry. Platinic chloride hastens the dissolution of most pure metals. Zinc will only dissolve in acids when some " impurity " is added. The purer it is, the less the chemical action, from which it is inferred that chemically pure zinc is insoluble in pure dilute acid.

Nitric acid, too, when pure will only slowly dissolve such metals as silver, copper, bismuth, cadmium and mercury in the pure state. As it is the normal development of nitrous vapours which hastens the reaction, the presence of an oxidising body to destroy the catalyst prevents the dissolution.

The solution of certain compounds, too, is hastened by the presence of traces of other material, each compound having its own dissolution catalyst.

CRYSTALLISATION.

The action of crystal nuclei in determining the crystallisation of supersaturated solution and supercooled liquids is essentially a catalytic—perhaps a special kind of autocatalytic—process. The subject possesses technical importance in connection with devitrification. Closely allied to this is the catalytic influence of certain metals upon the changes of state in the cooling of cast iron. Further consideration of these subjects, however, cannot be attempted here, as opening impracticably large fields of discussion.

INDEX

A.

W.

Z.